ABSTRACT: A series of 4,4′–π–conjugated–2,2′–bipyridine chromophores (MS 1–8) were synthesized and their photophysical and thermal properties studied. The title ‘push-pull’ chromophores, except MS 1, are integrated with both alkoxy and alkylamino donor functionalities which differ in their donation capabilities. The oligophenylenevinylene (OPV) chromophores MS 4–8 are associated with a π–extended backbone in which the position and the number of alkoxy donors have been systematically varied. All the studied systems possess a D–π–A–A–D π–D dyad archetype in which the A–A is the central 2,2′–bipyridine acceptor core which is electronically attached with the donor termini through π–linkers. The fluorescence quantum yields of the synthesized chromophores are found to be sensitive to the molecular archetype and the solvent medium. Among the eight fluorophores described in this chapter, compound MS 5 exhibits fluorescence in the solid state too. The modulating effect of the nature, position and number of donor functionalities on the optical properties of these classes of compounds has further been comprehended on the basis of DFT and TD–DFT computation in solvent model.

• 4.1. INTRODUCTION

In the contemporary era, fluorescence has turned out to be an indispensable analytical technique in the various branches of science, most prominently, in the fields of analytical, biological and medical sciences etc.¹ Among the diverse classes of organic π–systems, the materials that absorb electromagnetic radiation by virtue of an intramolecular charge transfer (ICT) and emit from the corresponding photoexcited state, are the most fascinating because of their notable applications in the field of molecular electronics, integrated photonic devices and nonlinear optics (NLO),² etc. The elegant fabrication of an electron donor-acceptor (DA) or ‘push-pull’ architecture can be carried out via the electronic unification between the donor and acceptor mesomeric units in a chromophore which is in turn, linked with spontaneous charge redistribution between the functionalities (ICT). Consequently, much research interest has been paid to the design and synthesis of diverse classes of DA-type fluorescent probes, associated with brilliant
photophysical behaviors; some typical examples of such fluorescent probes being acridine,\textsuperscript{3} fluorescein,\textsuperscript{4} cyanine,\textsuperscript{5} rhodamine,\textsuperscript{6} coumarin,\textsuperscript{7} BODIPY,\textsuperscript{8} squarines,\textsuperscript{9} oligophenylenevinylene (OPVs),	extsuperscript{10} etc.

The beauty of organic chemistry to devise a wide variety of chromophores lies in the disconnection approach, wherein the nitrogen containing heterocycles act as very promising building blocks to synthesize diverse classes of strongly emissive materials.\textsuperscript{11} The 2,2′–bipyridine derivatives are endowed with an extensive coordination / supramolecular chemistry.\textsuperscript{12} However, in photoscience, it is advantageous to employ this N–heterobiaryl compound because of the fact that, easy derivatization of the pyridine rings offers introduction of an assorted class of donor end-capping functionalities to tune the optical properties of the relevant 2,2′–bipyridine based dyads. Since the past two decades, many research groups including Le Bozec, Beer, Abbotto and others have accounted for the diverse end-capped 2,2′–bipyridine chromophores with moderate to strong emission responses.\textsuperscript{13–15} Recently, Ajayaghosh and co-workers have exemplified the chemo-sensing properties of the 2,2′–bipyridine based luminophores.\textsuperscript{16} The transition metal complexes of the 2,2′–bipyridine based DA systems are of topical interest due to their potential applicability in octupolar nonlinearity.\textsuperscript{17} The heteroleptic bis–thiocyanato ruthenium complexes, bearing a TiO\textsubscript{2} anchoring 2,2′–bipyridine ligand along with another auxiliary 2,2′–bipyridine ligand (known as antenna), have proved to be very promising photosensitizers for building high–performance dye sensitized solar cell modules.\textsuperscript{18}

The exciting photophysical responses of the 2,2′–bipyridine based DA systems and their transition metal complexes have captured our attention.\textsuperscript{19} The bipyridine based chromophores reported so far, are either symmetrically (point group = \textit{C\textsubscript{i}}) or disymmetrically (point group = \textit{C\textsubscript{1}}) substituted with alike donor functionalities (for example alkylamino etc.) whereas, photophysical properties of the associated hetero-donor systems have been less explored. In this chapter, a series of \textit{styryl–} and \textit{bistyryl–} 2,2′–bipyridine luminophores (\textbf{MS 2–8}, Chart 1) functionalized with both the alkoxy and amino functionalities in \textit{C\textsubscript{i}} symmetrical fashion and their photophysical properties have been demonstrated. The prototype of the synthesized dyads is of D–\pi–A–A–\pi–D (D = donor, A = acceptor) in which the bipyridine moiety acts as the central acceptor core to
join the terminal donor functionalities through vinylene linkers. The Horner–Wadsworth–Emmons reaction (HWE) has been exclusively used so as to introduce electron donating groups into the bipyridine central acceptor core unit. The photophysical properties of the synthesized chromophores (MS 1–8, Chart 1) are compared with four reported dyes namely, (a) the blue OLED dye 4,4’-bis(2,5-dimethoxystyryl)-2,2’-bipyridine (known as N945L) reported by Nazeeruddin and Grätzel;\textsuperscript{15a} (b) 4,4’-bis(4-dibutylaminostyryl)-2,2’-bipyridine (named as HLB 1 in this chapter)\textsuperscript{13d} and 4,4’-bis(4-(4-dibutylamino styryl)styryl)-2,2’-bipyridine (named as HLB 2 in this chapter)\textsuperscript{13h} reported by Le Bozec; and the 4,4’-bis(4-(2,5-dimethoxystyryl)styryl)-2,2’-bipyridine (named as TM 6) reported by us\textsuperscript{19a} (see Chart 1). A pragmatic observation points up that the introduction of the amino donor functionalities to N945L / TM 6 or alkoxy donors to HLB 1 / HLB 2 have induced a significant alteration of the photonic responses in the present chromophores. In addition, the position of the alkoxy functionalities attached to the conjugated backbone of the OPV derivatives, MS 4–8, greatly influences their photophysical properties. Furthermore, a thorough computational analysis in the level of
Density Functional Theory (DFT) in solvent model was applied to scrutinize the effect of donor positions on the geometrical and electronic parameters of the reference and the synthesized chromophores. All the synthesized π–conjugated molecules MS 1–8 fluoresce at room temperature with large Stokes shift while the emissive behavior of the OPV chromophores MS 4–8 epitomizes a large sensitivity to the solvent polarity. Amongst eight fluorescent compounds accounted here, the compound, MS 5 is emissive in the solid state too.

Scheme 1. Convenient synthetic protocols to access the symmetrical bipyridine chromophores.

- **4.2. RESULTS AND DISCUSSION**
  - **4.2.1. Synthesis and characterization**

The bench-top syntheses of the 4,4′–π–conjugated–2,2′–bipyridine chromophores can be accomplished via highly efficient synthetic protocols (see Scheme 1). The symmetrically substituted 2,2′–bipyridine derivatives (point symmetry =C_i) can, indeed, be easily derived either through (a) a Knoevenagel type reaction between the doubly deprotonated 4,4′–dimethyl–2,2′–bipyridine (1) and suitable aromatic aldehydes or (b) a Horner–Wadsworth–Emmons (HWE) reaction between the bis–phosphonate (2) and aromatic aldehydes. The Knoevenagel type reaction in fact, triggers at the acidity of the 4–picolyl
protons of the bipyridine starting precursor (1). A two-step synthetic approach that was developed, entailed the deprotonation of 1 by a strong base e.g. lithium diisopropylamide (LDA) at low temperature followed by nucleophilic addition of the resulting carbanion to an aromatic aldehyde to form a secondary alcohol. The resulting alcohol is then dehydrated, usually, by pyridinium p-toluene sulfonate (PPTS) to convert it to the corresponding alkene (Scheme 1). An alternative one-step protocol which directly yielded the desired alkenes, involved heating of a mixture of 1 and an aromatic aldehyde in presence of a strong and hindered base e.g. KOBu in DMF. The donor end-capping functionalities in the present bipyridine chromophores (MS 1–8) were, however, introduced by the HWE protocol due to its better performance (high yield, E–selectivity etc.) in comparison with the two other methodologies as described in Scheme 1. Also, the conventional Wittig pathway was avoided due to the undesired trouble with the coproduct, triphenylphosphine oxide, during work-up and purification. The key intermediate of the HWE pathway is the phosphonate 2 which has been extensively used in literature to synthesize a diverse class of symmetrically substituted 2,2′-bipyridine chromophores. The concerned intermediate (2) was easily derived from the corresponding halomethyl derivatives through an Arbuzov reaction. An initial attempt to
Table 1. Synthesis of the 4-styrylbenzaldehydes.

<table>
<thead>
<tr>
<th>Phosphonate</th>
<th>ArCHO</th>
<th>Bromostilbenes</th>
<th>Styrylbenzaldehydes</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>OHC-NMe</td>
<td>7a 87%</td>
<td>10a 87%</td>
</tr>
<tr>
<td>8</td>
<td>OHC-NBu₂</td>
<td>5b 91%</td>
<td>11a 91%</td>
</tr>
<tr>
<td>8</td>
<td>OHC-MeO</td>
<td>7b 94%</td>
<td>12a 94%</td>
</tr>
<tr>
<td>9</td>
<td>OHC-NBu₂</td>
<td>5a 92%</td>
<td>13a 92%</td>
</tr>
<tr>
<td>9</td>
<td>OHC-MeO</td>
<td>5b 92%</td>
<td>14a 92%</td>
</tr>
<tr>
<td>9</td>
<td>OHC-NMe</td>
<td>7b 88%</td>
<td>15a 88%</td>
</tr>
</tbody>
</table>

brominate 1 through a radical mechanized reaction route (NBS/benzoylperoxide or AIBN) was unsatisfactory for obtaining 4,4'-bis-bromomethyl-2,2'-bipyridine. However, the corresponding chloromethyl derivative, 1a, was used throughout the present work which had been synthesized following an efficient synthetic protocol.
developed by Fraser and co-workers. The concerned two-step approach involved deprotonation of 1 with LDA and trapping of the resulting carbanion with chlorotrimethylsilane, followed by subsequent chlorination with hexachloroethane in presence of a dry fluoride source, cesium fluoride (CsF). The aldehydes used in the present study were not commercially accessible and therefore, were synthesized as described in the following sections.

The anilines 3a–b were alkylated in presence of the suitable electrophiles in \( N \)-methylpyrrolidinone (NMP)–DMF solvent system to obtain the desired \( N,N \)-dialkylanilines (4a–b, 6a–b) in good yield (Scheme 2). Our experimental observation suggested that usage of 10% \( N \)-methylpyrrolidinone (NMP) in DMF as solvent afforded the corresponding \( N,N \)-dialkylanilines in better yield compared to other reagents and/or solvent combinations such as \( K_2CO_3 \)–acetone/ethanol/DMF/THF or \( NaH \)–THF/DMF etc. Subsequently, the Vilsmeier–Haack formylation of the \( N,N \)-dialkylanilines (4a–b, 6a–b) converted them to the corresponding benzaldehydes (5a–b, 7a–b) with excellent para–selectivity.

The \( \pi \)-conjugated benzaldehydes bearing different substitutions were obtained through a two–step synthetic approach as depicted in Table 1. The introduction of different donor functionalities in the corresponding aldehydes 10b–15b was executed via the appropriate selection of the starting materials. The usage of an alkoxy derivatized phosphonate precursor (9) allowed the introduction of the alkoxy functionalities in the formylated phenyl rings. At the outset, the HWE reaction between the appropriate phosphonate (8–9) and the alkylaminobenzaldehydes (5a–b, 7a–b) afforded the corresponding bromostilbenes (10a–15a) in excellent yield with the \( E \)–selectivity of the C=C bonds. Subsequent lithium–halogen exchange reaction followed by electrophilic quenching with dimethylformamide converted the bromostilbenes (10a–15a) to the corresponding benzaldehydes (10b–15b) in moderate to good yields (Table 1).

4.2.2. NMR spectroscopy

The molecular structures of all the synthesized bipyridine chromophores (MS 1–8) were unambiguously determined through NMR (\( ^1H \) and \( ^{13}C \)) and mass (LC–MS and MALDI–TOF/TOF) spectroscopy. The presence of only one set of \( ^1H \) and \( ^{13}C \) signals in the NMR spectra evidently demonstrates the symmetrical nature of the chromophores. The \( ^1H \)
NMR resonances of the pyridine rings and that of the vinylic protons for the chromophores, MS 1–8 are summarized in Table 2. The pyridine–H\textsubscript{6,6}' protons, being largely deshielded by the adjacent electronegative nitrogen atom appear as the most downfield shifted signal while the pyridine–H\textsubscript{5,5}' protons, owing to their meta-orientation with respect to the nitrogen atom, resonate in the benzene region (Table 2). The downfield shift of the pyridine–H\textsubscript{3,3}' protons compared to the pyridine–H\textsubscript{5,5}' protons can be attributed to the transoid- arrangement of the two pyridine rings in the relevant bipyridine chromophores.\textsuperscript{13f} All the vinylic C=C bonds are found to be in E-geometry as indicated by the splitting of each of the CH resonances by the neighbouring protons with a \( ^3J_{HH} \) coupling constant of \( ca. \) 16 Hz. However, no trace of the Z-isomer has been signified in the relevant \(^1\text{H}\) NMR spectra. A comparison between the \(^1\text{H}\) NMR signals due to the aromatic protons of the open chain amino donor end-capped chromophore MS 2 (dibutylamino donor) and its cyclic analogue i.e. MS 3 (pyrrolidine donor) reveals that the protons attached ortho- to the amino functionalities have a larger chemical shift in case of MS 2 as compared to MS 3 (see Figure 1). The figure herein evidently shows that all the aromatic protons of the two chromophores, except those attached to the ortho-position with respect to the amino functionality (H\textsubscript{11,11'}), have almost similar chemical

Table 2. Selected \(^1\text{H}\) NMR chemical shifts for MS 1–8. All the spectra were recorded at 400 MHz working frequency in CDCl\textsubscript{3} at 298±2 K. The resonances are reported in ppm with respect to the TMS signal.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Py–H\textsubscript{6,6}'\textsuperscript{a}</th>
<th>Py–H\textsubscript{3,3}'</th>
<th>Py–H\textsubscript{5,5}'\textsuperscript{b}</th>
<th>CH=CH\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS 1</td>
<td>8.625 (d)</td>
<td>8.48 (s)</td>
<td>7.35–7.34</td>
<td>7.41 (d), 6.91 (d)</td>
</tr>
<tr>
<td>MS 2</td>
<td>8.635 (d)</td>
<td>8.48 (d)</td>
<td>7.44–7.43</td>
<td>7.75 (d), 7.05 (d)</td>
</tr>
<tr>
<td>MS 3</td>
<td>8.605 (d)</td>
<td>8.46 (s)</td>
<td>7.43–7.41</td>
<td>7.75 (d), 6.98 (d)</td>
</tr>
<tr>
<td>MS 4</td>
<td>8.695 (d)</td>
<td>8.56 (s)</td>
<td>7.42–7.40</td>
<td>7.50 (d), 7.47 (d), 7.14 (d), 7.00 (d)</td>
</tr>
<tr>
<td>MS 5</td>
<td>8.680 (d)</td>
<td>8.56 (s)</td>
<td>7.42–7.40</td>
<td>7.50 (d), 7.47 (d), 6.94 (d)</td>
</tr>
<tr>
<td>MS 6</td>
<td>8.675 (d)</td>
<td>8.52 (s)</td>
<td>7.46–7.45</td>
<td>7.80 (d), 7.28 (d), 7.20 (d), 7.10 (d)</td>
</tr>
<tr>
<td>MS 7</td>
<td>8.675 (d)</td>
<td>8.51 (s)</td>
<td>not resolved</td>
<td>7.80 (d), 7.37 (d), 7.21 (d)</td>
</tr>
<tr>
<td>MS 8</td>
<td>8.675 (d)</td>
<td>8.51 (s)</td>
<td>not resolved</td>
<td>7.80 (d), 7.49 (d), 7.32 (d), 7.20 (d)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \(^3J_{HH} = 4\) Hz except in MS 5 for which \( J = 8\) Hz; \textsuperscript{b} could be either doublet or doublet of doublet; \textsuperscript{c} coupling constant \( (^3J_{HH}) \approx 16\) Hz, for MS 5 and MS 6 one signal is overlapped with others and could not be separately detected. MS 1–3 contains only two vinylic protons in their molecular structure.
shifts. The $^{11,11'}$ nuclei of MS 2 resonate at $\delta$ 6.50 while those corresponding to MS 3 has been upfield shifted to $\delta$ 6.27 in the NMR spectra. This is clearly indicative of a more shielded environment around the relevant protons in the cyclic amino donor end-capped chromophore MS 3 in comparison to the open chain analogue MS 2. The electron donating mesomeric effect of the amino groups makes the corresponding ortho– position of the phenyl rings more electron rich thereby exerting greater shielding effect on the relevant protons ($^{11,11'}$). Thus, it can be aptly said that the pyrrolidine moiety has a greater donation capability than the corresponding open chain amino donor, dibutylamine. The concerned protons in the other open chain/cyclic amino donor pairs viz. MS 4/MS 5 and MS 7/MS 8 resonates at $\delta$ 6.55/6.31 and $\delta$ 6.53/6.31 respectively. A similar trend has also been observed for resonances of the carbon atoms ortho– to both the amine and the alkoxy functionalities (e.g. $^{11,11'}$ in MS 2/MS 3) in the relevant $^{13}$C NMR spectra which display upfield shifted signals in the pyrrolidine end-capped chromophores as compared to the dibutylamino end-capped systems.

Figure 1. $^1$H NMR signals of MS 2 and MS 3 in the aromatic region of the spectra (400 MHz, CDCl$_3$, 298 ±2 K) showing the difference in chemical shift of the proton adjacent to the amino donor ($^{11,11'}$). S = solvent signal.
Table 3. Summary of the optical data of the synthesized chromophores (MS 1–8).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon \ (\pm 500-1000) ) (L.mol(^{-1}).cm(^{-1}))</th>
<th>( \lambda_{\text{em}} ) (nm)</th>
<th>( \Phi_{\text{em}} ) (±0.1)</th>
<th>( \Delta \nu_{\text{em}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS 1</td>
<td>Toluene</td>
<td>390</td>
<td>448</td>
<td>0.05</td>
<td>3320</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>393</td>
<td>485</td>
<td>0.09</td>
<td>4827</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DCM</td>
<td>396</td>
<td>498</td>
<td>0.09</td>
<td>5172</td>
<td></td>
</tr>
<tr>
<td>MS 2</td>
<td>Toluene</td>
<td>392</td>
<td>472</td>
<td>0.09</td>
<td>4324</td>
<td></td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>396</td>
<td>507</td>
<td>0.17</td>
<td>5529</td>
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</tr>
<tr>
<td></td>
<td>DCM</td>
<td>399</td>
<td>60000</td>
<td>0.20</td>
<td>6301</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MeCN</td>
<td>397</td>
<td>550</td>
<td>0.03</td>
<td>7007</td>
<td></td>
</tr>
<tr>
<td>MS 3</td>
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<td>480</td>
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<td>560</td>
<td>0.04</td>
<td>6653</td>
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<tr>
<td>MS 4</td>
<td>Toluene</td>
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<td>114000</td>
<td>0.55</td>
<td>5931</td>
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<tr>
<td></td>
<td>THF</td>
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<td>100000</td>
<td>0.64</td>
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<td></td>
<td>DCM</td>
<td>413</td>
<td>95000</td>
<td>0.37</td>
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<td></td>
<td>MeCN</td>
<td>405</td>
<td>585</td>
<td>0.07</td>
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<tr>
<td>MS 5</td>
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<td>427</td>
<td>552</td>
<td>0.85</td>
<td>5303</td>
<td></td>
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<tr>
<td></td>
<td>THF</td>
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<td>630</td>
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<tr>
<td></td>
<td>DCM</td>
<td>430</td>
<td>122000</td>
<td>0.21</td>
<td>8150</td>
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<tr>
<td></td>
<td>MeCN</td>
<td>428</td>
<td>603</td>
<td>0.17</td>
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<tr>
<td>MS 6</td>
<td>Toluene</td>
<td>436</td>
<td>116000</td>
<td>0.66</td>
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<tr>
<td></td>
<td>THF</td>
<td>437</td>
<td>99000</td>
<td>0.81</td>
<td>5492</td>
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<tr>
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<td>95000</td>
<td>0.65</td>
<td>5902</td>
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<tr>
<td></td>
<td>MeCN</td>
<td>433</td>
<td>641</td>
<td>0.19</td>
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<tr>
<td>MS 7</td>
<td>Toluene</td>
<td>432</td>
<td>100400</td>
<td>0.63</td>
<td>4966</td>
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<tr>
<td></td>
<td>THF</td>
<td>431</td>
<td>96000</td>
<td>0.62</td>
<td>6281</td>
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<tr>
<td></td>
<td>DCM</td>
<td>435</td>
<td>87000</td>
<td>0.35</td>
<td>7556</td>
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</tr>
<tr>
<td></td>
<td>MeCN</td>
<td>430</td>
<td>650</td>
<td>0.03</td>
<td>7871</td>
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<tr>
<td>MS 8</td>
<td>Toluene</td>
<td>445</td>
<td>131000</td>
<td>0.59</td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>DCM</td>
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<td>0.23</td>
<td>7170</td>
<td></td>
</tr>
<tr>
<td></td>
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<td>428</td>
<td>640</td>
<td>0.07</td>
<td>7740</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) \( E_T(30) \) values of the used solvents are as follows: Toluene (33.9), THF (37.4), DCM (40.7), MeCN (45.6). \( ^b \) Data is represented as the average of five measurements. In cases where no data are reported, this is due to low solubility. \( ^c \) The solutions were excited at the corresponding lowest energy absorption maxima. \( ^d \) Fluorescence relative quantum yield of the compound MS–1 was measured using quinine sulfate (in 1N H\(_2\)SO\(_4\)) as the reference (\( \Phi_{\text{em}} = 0.545 \)) and that of the rest of the compounds (MS 2–8) were performed using DCM–Pyran as the reference in MeOH (\( \Phi_{\text{em}} = 0.435 \)). Comparable result was obtained using fluorescein (in 0.1N NaOH) as the standard substance too. Optically matched solutions (OD ≈ 0.05) of the samples and that of the standards were excited at identical operating condition. The data is presented as an average of two measurements. \( ^e \) Stokes shift \( \Delta \nu = \nu_{\text{abs}} - \nu_{\text{em}} \).
4.2.3. Steady-state absorption and emission properties

(a) Nature of substituents. The steady-state one photon absorption and emission properties of the synthesized chromophores MS 1–8 have been investigated in four different solvents (see Table 3 and Figure 2). The nature and position of the donor functionalities in the molecular conjugated backbone and the polarity of the fluid medium in which the compounds are dissolved, were observed to have a profound effect on the absorption and emission properties of the synthesized chromophores. As shown in Figure 2, broad structureless bands of the absorption and emission spectra in the visible region are the chief characteristic features of all the chromophores in the present study. The molar extinction coefficient (ε) of the lowest energy absorption band of all the chromophores is fairly high and though it varies only slightly with the solvent polarity, the nature of the donor functionality has an immense influence on it (see Table 3). The low solubility of MS 1 precluded measurement of the molar absorptivity with a better accuracy. The origination of the lowest energy band in the absorption spectra of MS 1–8, however, is due to an intramolecular π→π* charge transfer (ICT) from the donor based molecular orbitals to the acceptor (pyridine) based molecular orbitals in the relevant dipolar chromophores which in fact, is firmly affirmed owing to the sensitivity of the relevant absorption band on the solvent polarity (see Table 3). In addition, the ICT band maxima undergoes a bathochromic shift by ca. 15 nm for the pyrrolidine end-capped (cyclic amino donor) chromophores as compared to that of the dibutylamino (open chain amino donor) analogues viz. MS 2/MS 3, MS 4/MS 5 and MS 7/MS 8 in the same solvent medium (Table 3). The rationale for this observation might be due to the greater donation capability of the cyclic pyrrolidine donor compared to the open chain dibutylamino donor. This context has already been discussed in the previous section by the up-field shift of the ¹H NMR signal of the proton attached ortho– to both the amino and the methoxy functionalities in the relevant chromophores (vide supra).

Upon excitation at the lowest energy absorption maxima, the chromophores MS 1–8 exhibit a bright fluorescence at room temperature with a large Stokes shift from the relevant absorption maxima (see Table 3). The positions of the corresponding emission maxima are found to be independent of the excitation wavelength thereby indicating that the photoluminescent nature of the synthesized chromophores holds concurrence with
Kasha’s law of photochemistry. Likewise, an excellent overlapping of the excitation spectra with the relevant lowest energy absorption maxima for the title chromophores MS 1–8 has been observed (see Figure 2a and 2b). The effect of solvent polarity on the emission property of the present chromophores is found to be more pronounced as compared to the absorption spectra (see Table 3). For instance, increasing the solvent polarity from toluene to DCM induces a bathochromic shift of ca. 6–7 nm in the electronic absorption spectra of the first homologues MS 1–3, whereas the corresponding emission maxima are red–shifted by about 50–63 nm due to the same polarity increment. This observation is indicative of the fact that the photo–excited state of the concerned luminophores is markedly polar than the ground electronic state. The effect of solvent polarity on the emission properties is even more profound in case of the OPV derivatives MS 4–8 compared to the styryl– analogues MS 1–3 (see Table 3 and Figure 2c). For example, alteration of the solvent polarity from toluene to DCM brings about 61–63 nm bathochromic shift of the emission maxima for the first homologues MS 2–3 but as large as 104–110 nm shift of the emission maxima to the longer wavelength has been observed in case of the second homologues MS 4–5 under the same polarity deviation (see Table 3) and the emission color changes from deep green to orange-red (see Figure 2c). The general tendency of the dipolar fluorophores is the shifting of their emission maxima to lower energy (longer wavelength) as they approach more polar solvents owing to the fact that they exhibit a large change in dipole moment during the photo–excitation process. Thus, the excited state is stabilized by the solvent molecules via solvation through the dipole–dipole interactions and this reduces the energy gap between the emitting state and the ground electronic state of the fluorophore in the more polar solvents. However, on increasing the solvent polarity from DCM to acetonitrile, the hipsochromic shift of the emission maxima by ~60 nm for MS 4–5 and ~ 20 nm for MS 8 in contrast to the 43 nm and 2 nm bathochromic shift of the same for MS 6 and MS 7 respectively is not fully understood. The variation in the photoluminescent quantum yield of all the title fluorophores were examined with the same set of solvents and are compiled in Table 3. The OPV derivatives, MS 4–8, exhibit brighter fluorescence in comparison with the first homologues, MS 1–3 (see Table 3). The relative quantum yield of the title chromophores is however, strongly dependent on the fluid medium and an irregular alteration of the
Figure 2. Normalized absorption (solid lines, concentration of the samples being \( \sim 1 \times 10^{-5} \) M), emission (dashed lines) and excitation spectra (overlapped with the absorption spectra) together with the computed vertical excitation energies (stick lines) of (a) MS 1–3 and (b) MS 4–8 in DCM at 298±2K. All the solutions were excited at the lowest energy absorption maxima. Heights of the vertical lines have been adjusted so as to obtain a viewing lucidity; the relative heights are however in scale. (c) Photographs showing photoluminescence behavior of the MS 1–8 in four different solvents illuminated under an UV lamp (excitation 365 nm) in the dark.
same with the solvent polarity is observed (see Table 3). The sensitivity of the absorption and emission properties of the title choromophores to the fluid medium evidently portrays the ‘push–pull’ architecture of MS 1–8. Apart from all the above mentioned observations, some unique spectroscopic features were explored while altering the substituents and these have been addressed in the following sections, taking into account the spectral behavior of N945L, HLB 1, HLB 2 and TM 6.

The 4–dibutylaminostyryl chromophore HLB 1 absorbs at 401 nm ($\varepsilon = 65000 \text{ L.mol}^{-1}\text{cm}^{-1}$) due to an ICT and emits at 497 nm ($\Phi_{\text{em}} = 0.230$) from the corresponding excited state in DCM. Similarly, the 2,5–dimethoxystyryl chromophore N945L absorbs and emits at 358 nm ($\varepsilon = 40410 \text{ L.mol}^{-1}\text{cm}^{-1}$) and 450 nm ($\Phi_{\text{em}} = 0.430$) respectively in DCM involving the ground and excited ICT states. However, the chromophore MS 2 which was designed and synthesized by introducing both methoxy as well as dibutylamino donor substituents together in the same ring positions as in HLB 1 and N945L, exhibits a modulated photophysical behavior compared to the two concerned reported chromophores HLB 1 and N945L. A comparison of the photophysical parameters of MS 2 with that of its parents HLB 13d and N945L15a shows that the ground state property of MS 2 is comparable with that of HLB 1. Even though it was expected that the coexistence of the amino and the alkoxy donor functionalities in the same chromophore would lead to a bathochromic shift of the corresponding charge transfer band, this was not actually found to be the case with MS 2. Our observation rather suggests that, owing to the greater donation capability of the amino donor functionality, it has a dominant contribution in the respective $\pi(\text{phenyl})\rightarrow\pi^*\text{(pyridine)}$ charge transfer interaction since the optical response of the ground state of MS 2 resembles that of HLB 1 and not of N945L. Thus, the presence of methoxy groups together with the amino substituent has a little influence on the electronic absorption properties of the chromophore. However, a significant variation in the emission color is observed for MS 2 as compared to HLB 1 or N945L. The chromophore MS 2 exhibits a deep green emission at 533 nm in DCM which occurs at a considerable longer wavelength than the emission due to HLB 1 (497 nm) or N945L (450 nm). The addition of the amino functionality to N945L or two methoxy donors to HLB 1 generates MS 2 which exhibits a significant weaker fluorescence compared to N945L though the
fluorescence quantum yields of MS 2 and HLB 1 are reasonably comparable. Hence, it can be said that presence of both the amino and methoxy functionalities in the same chromophore has more profound effect on the emitting state compared to the ground state of the aforementioned luminophores. At this juncture, it is worth mentioning that the position of the donor functionalities plays a crucial role for the variation of the quantum efficiency in the 4,4′–π–conjugated–2,2′–bipyridine fluorophores.

The absorption and emission behaviour of the OPVs, HLB 2, TM 6 and MS 4 follow an almost similar trend as the first homologues viz. HLB 1, N945L and MS 2 respectively. In contrast to the first homologues, where the donor substituted phenyl ring and the pyridine acceptor sub–chromophore are separated by an olefinic spacer, the corresponding OPV chromophores HLB 2, TM 6 and MS 4 are associated with an extended π–skeleton involving an additional styryl spacer in between the donor–acceptor fragments. For a convenient discussion in the text, the two phenyl rings of the OPV chromophores are named as ring–A and ring–B (see Chart 1). The absorption and emission spectra of HLB 2 consisting of the dibutylamino donor functionality at ring–B (R₃ = NBu₂, see Chart 1) are characterized by the relevant maxima at 420 nm (ε = 78000 L.mol⁻¹.cm⁻¹) and 598 nm (Φₑᴍ = 0.700) respectively in DCM with a Stokes shift of 7087 cm⁻¹. The OPV chromophore TM 6 bearing two methoxy functionalities at the 2,5–positions of ring–B has recently been reported by us. This chromophore exhibits an absorbance maximum at 380 nm (ε = 45900 L.mol⁻¹.cm⁻¹) and emission maximum at 488 nm (Φₑᴍ = 0.730) in DCM with a Stokes shift of 5824 cm⁻¹. Under similar experimental conditions, the hybrid chromophore MS 4, which comprises both the –NBu₂ and the –OMe functionalities in the same positions as in HLB 2 and TM 6, absorbs at 413 nm (ε = 95000 L.mol⁻¹.cm⁻¹) due to an ICT and exhibits an orange–red emission (λₑᴍ = 644 nm, Φₑᴍ = 0.365) with a very large Stokes shift (8685 cm⁻¹) from the relevant absorption maximum. Thus, alike the first homologues, coexistence of the methoxy donors along with the dibutylamino groups in MS 4 has a very little influence on the absorption wavelength. The molar extinction coefficient of the ICT band of MS 4 is however, significantly larger than that of HLB 2. The influence of methoxy donors is found to be rather dramatic on the fluorescence behavior of the relevant OPV chromophores. It has been observed that compared to HLB 2 and TM 6, the fluorophore MS 4 emits at a
considerably longer wavelength, but with almost half quantum efficiency. In other words, both the approaches, *viz.* (a) attaching methoxy donors to **HLB 2** at ring–B or (b) introducing amino donor to **TM 6** at ring–B render a significant bathochromic shift of the emission wavelength in the resultant chromophore with the concomitant diminution of the fluorescence brightness. In this context, some important experimental observations need to be addressed. The fluorescence quantum yields of both the chromophores, **HLB 2** and **TM 6** are almost similar ($\Phi_{\text{em}} = 0.700$ vs 0.730 respectively) which signifies that the fluorescence brightness of the OPV chromophores, containing donor functionalities at the ring–B, is not much sensitive to the nature of the donor, as far as the chromophore is associated with similar type of electron pushing moiety. An almost identical situation is observed with the OPV chromophores containing two methoxy donors at the 2,4– and 2,5– positions of ring–B ($\Phi_{\text{em}} = 0.700$ vs 0.730 respectively) thereby indicating that the quantum efficiency of the related chromophores is independent of the position of the donor functionalities.\(^{19a}\) However, the effect of nature and position of the donor sub–chromophores on the fluorescence brightness of the first homologues is remarkably different. The divergence in quantum yield of **HLB 1** ($\Phi_{\text{em}} = 0.230$) and **N945L** ($\Phi_{\text{em}} = 0.430$) is noteworthy.

(b) **Position of substituents.** A careful analysis of the optical data presented in Table 3 reveals some interesting features. The influence of the nature of donor and conjugation length on the photophysical behavior of the bipyridine chromophores has already been addressed in the previous section. The OPV chromophores **MS 4**, **MS 6** and **MS 7** were designed and synthesized in order to investigate the outcome of varying the position and number of alkoxy donors on the absorption and emission properties of the relevant chromophores. In **MS 4**, two methoxy donors are attached with the ring–B at 2,5– positions along with the dibutylamino donor at 4–position (Chart 1). In case of **MS 6**, two butyloxy donors were used for the aid of solubility in contrast to the two methoxy donors in **MS 4**. Moreover, the alkoxy donors have been moved to ring–A (2,5– positions) in case of **MS 6** as compared to **MS 4**, the total number of donor units being same for both the chromophores. The alkyl chain length in the alkoxy donors is not expected to alter the $+I$ effect to a very significant extent and therefore, spectroscopic features of any chromophore bearing methoxy or butyloxy donor functionalities would be almost...
identical. Hence, the variation in the absorption and emission properties of MS 4 and MS 6 is administered only by the position of the alkoxy donors in the conjugation backbone of the relevant chromophores. The absorption due to an intramolecular charge transfer in

![Figure 3. Solid state absorption (black) and emission (red) spectra of MS 5 at room temperature (KBr pellet, arbitrary concentration). The inset shows photographs of the relevant KBr pellet and bulk sample illuminated with a 365 nm UV lamp.](image)

MS 6 (442 nm in DCM) is shifted to longer wavelength by ca. 30 nm compared to that in MS 4 (413 nm in DCM) and the reason behind this might probably be due to the greater extent of conjugation between the alkoxy donor and pyridine acceptor functionalities in MS 6 due to a smaller separation between the donor-acceptor moieties. On the contrary, the emission spectrum of MS 6 exhibits almost 45 nm hypsochromic shift compared to MS 4 in DCM and furthermore, the fluorescence quantum yield of MS 6 is considerably larger than that of MS 4 (Φem = 0.65 for MS 6 and 0.37 for MS 4 in DCM). The chromophores MS 7 and MS 8 bear the highest number of donor units among all the compounds discussed in this chapter. Most surprisingly, in spite of attaching extra alkoxy donors with the ring–B of MS 6, a further shift of the ICT absorption to the longer wavelength has not been induced but instead a hypsochromic shift of ca. 7 nm of the relevant band position is observed for MS 7. The emission properties of the luminophores MS 4 and MS 7 are almost similar except in MeCN in which the former exhibits yellow emission but the latter exhibits red emission (see Table 3 and Figure 2c).
• **4.2.4. Solid state emission of MS 5**

Among all the studied ‘push-pull’ chromophores in the present work, MS 1–8, the compound MS 5 fluoresces even in the solid state. The solid state absorption and emission spectra of the pertinent compound were recorded in dilute KBr matrix and the relevant spectra are presented in Figure 3. The absorption spectrum is characterized by a broad band centered at 442 nm which is slightly red-shifted with respect to the absorption maxima of the relevant dyad in dissolved media (see Table 3). The bathochromic shift of the absorption maximum in condensed phase as compared to that of the solution state is presumably due an aggregation. When excited at the relevant absorption maximum, the chromophore MS 5 exhibits orange emission with the maximum intensity at 614 nm (see Figure 3).

• **4.2.5. Computational analysis**

(a) General considerations. To gain insight into the effect of various substituents on the geometrical and electronic outcome of the 2,2’–bipyridine chromophores, Density Functional Theory (DFT) and Time Dependent DFT (TD–DFT) were applied on the synthesized compounds MS 1–8 along with HLB 1, N945L, HLB 2, TM 6, styryl– and bistyryl– derivatives without any donor substituent using the Gaussian09 program package. The fundamental aim of the current work is to understand the influence of the nature and position of the various donor functionalities on the electronic properties of the 4,4’–π–conjugated–2,2’–bipyridine dyads functionalized with two dissimilar donor units. As a result, more emphasis is given to the electronic structures of the studied systems instead of their geometrical parameters in this section. In a nutshell, we have made an attempt to draw a correlation between the structural and electronic aspects of the related systems. Our computational analysis begins with the styryl– and bistyryl– 2,2’–bipyridine skeleton without any donor functionality. In addition, computational investigation has been carried out with HLB 1, N945L, HLB 2 and TM 6 along with the synthesized dyads of the present work. Although the DFT analysis of N945L has already been reported, we reproduced the same with our own computational set-up for the purpose of ready comparison. A semi-empirical calculation on HLB 2 was earlier reported by Hernández and co-workers (named as SY187). However, the absence of any X-ray crystal structure for the dye molecules of the present work impelled us to optimize the
geometries of all the studied systems, which in fact, was accomplished using the CAM-B3LYP exchange–correlation hybrid functional together with the 6–31+g(d) basis set imposing $C_i$ symmetry constraint. As the donation strength of butyl and methyl groups is not supposed to differ much, all the butyl chains of the OPV derivatives (MS 4, MS 6 and MS 7) were truncated to the methyl groups in an attempt to reduce the number of basis functions and consequently to increase the computational speed. The relevant geometrical structures were modelled by applying the Self–Consistent Reaction Field (SCRF) under Polarizable Continuum Model (C–PCM) incorporating DCM as the solvent. For the purpose of ready comparison between the various computed parameters, an identical theoretical set-up was maintained throughout the course of the computational investigations. As the transoid– conformation is energetically more favorable for the free bipyridine derivatives, all the geometry optimizations were carried out on transoid– input structures and no attempt was made to optimize the cisoid– input geometries. The DFT computed HOMO and LUMO Frontier Molecular Orbitals (FMOs) of the chromophores MS 1–8 are presented in Figure 4. A scrutiny on the computer modelled structures of the studied systems reveals some common features such as, almost coplanar structures of the systems which are devoid of any alkoxy functionality, out–of–plane displacement of the phenyl rings bearing the alkoxy substituents from the planes containing the pyridine ring and the C=C vinylic bonds etc. Hence, these matters have not been individually addressed over again for the systems used in this study.

(b) Electronic aspects. An investigation on the electronic structures reveals that an almost similar type of localization and nature of HOMO and LUMO are retained among the individual homologues (see Figure 4), the only difference being in the energy of these FMOs, which in turn, depend on the system architecture. The HOMO of the relevant chromophores is associated with the in–phase and out–of–phase $\pi$–bonding combination and consists of major coefficients at the phenyl rings containing the donor substituents and at the C=C vinylic bonds. On the contrary, the LUMO of the model structures stems from the $\pi^*$–type combination of the molecular orbitals (MOs), mainly contributed by the C=C bonds and the two pyridine rings along with a sizeable coefficient on the C–C bond joining the two pyridine rings. The modulation of energy for the four occupied (HOMO–3, HOMO–2, HOMO–1, HOMO) and four virtual (LUMO, LUMO+1, LUMO+2, LUMO
Figure 4. Isodensity plots of HOMO and LUMO frontier molecular orbitals of the bipyridine chromophores MS 1–8 as computed by the CAM-B3LYP/6–31+g(d) level of theory (isodensity value = 0.02). The butyl chains of MS 4 and MS 6–8 were truncated to the methyl groups.
+3) molecular orbitals upon alteration of the core architecture in the studied systems is presented in Table 4. The HOMO−1 and HOMO occupied MOs of all the studied systems constitute an almost degenerate couple. Such pairs in 4,4′-distyryl-2,2’-bipyridine and 4,4′-bis(4-styrylstyryl)-2,2’-bipyridine which are devoid of any donor functionality are most stabilized among all the model structures and are computationally estimated at −7.524/−7.470 and −6.921/−6.897 eV respectively. A considerable destabilization of the HOMO and HOMO−1 by 1.153 and 1.180 eV respectively is observed on introduction of the −NBu2 functionality (HLB 1) with concomitant lowering of the HOMO−LUMO gap by 0.945 eV. An identical donor alteration from MS 2 to MS 3 results in destabilization of the HOMO as well as lowering of the $E_g$ value by 0.030 and 0.030 eV respectively for MS 3, thereby pinpointing to the greater electron pushing effect of the pyrrolidine donor compared to that of the −NBu2 functionality in MS 2. The HOMO of N945L (−6.99 eV) is stabilized by 0.660 eV with respect to HLB 1 ($E_{\text{HOMO}} = −6.33$ eV) and hence, the $E_g$ value of N945L is elevated by 0.390 eV as compared to HLB 1. This observation is in concurrence with the stronger donation propensity of the amino functionality in HLB 1 than the methoxy donor in N945L. However, when both the methoxy and the amino functionalities are positioned together in MS 2, an attenuation of the $E_g$ value by 0.130 eV with respect to HLB 1 is computed thereby signifying to the greater electron pushing influence of the mixed donor system, MS 2 as compared to the single donor systems N945L or HLB 1. Overall, a varying degree of destabilization of the HOMO−1 and HOMO occupied levels along with alteration of the HOMO−LUMO gap has been observed upon introduction of the donor substituents to the 2,2’-bipyridine core skeleton (see Table 4). The consequence of conjugation length on the electronic structure of the bipyridine dyads is evidently comprehended in the computer modelled structures. For example, expansion of conjugation from MS 3 to MS 5 results in destabilization of the HOMO by 0.11 eV and a sizable shrinking of the HOMO−LUMO gap by 0.40 eV in MS 5 with respect to MS 3. As depicted in Figure 4, the π-character of the two phenyl rings and that of the two C=C vinyl linkages of the OPV derivatives attribute to the HOMO, the extent of localization being dependent upon the position and number of alkoxy donors. For instance in MS 4, the HOMO has larger coefficients at ring−B and C=C linkage between rings A and B with a relatively smaller contribution from the ring A.
Modification of the dyad skeleton from MS 4 to MS 6 increases the localization on ring–A and a subsequent destabilization of the HOMO by 0.14 eV and a declination of the $E_g$ value by 0.110 eV with respect to MS 4 is computed. Further substitution at ring–B leads to a stabilization of the HOMO by 0.03 eV and an increment of the HOMO–LUMO gap by 0.03 eV in MS 7 with respect to MS 6. However, the nature of LUMO in all the OPV derivatives are almost similar and are attributed from the $\pi^*$–combinations with major localization on the bipyridine central acceptor core and on the 2,2’– C–C bond between the two pyridine rings. Thus, it is obvious that, the modification of the archetype of the $\pi$–conjugated 2,2’–bipyridine dyad systems offer a systematic variation of the orbital energies and the HOMO–LUMO gap which are the direct consequences of their photophysical responses. The computational parameters discussed in this section are carried forward in the next section to comprehend the various TD-DFT outputs.

**Table 4. Energy (eV) of four higher occupied (HOMO–3, HOMO–2, HOMO–1, HOMO) and four lower virtual (LUMO, LUMO+1, LUMO+2, LUMO+3) molecular orbitals of the studied systems as computed in CAM-B3LYP/6-31+G(d) level of Theory (in DCM). H = HOMO, L = LUMO.**

<table>
<thead>
<tr>
<th></th>
<th>H–3</th>
<th>H–2</th>
<th>H–1</th>
<th>H</th>
<th>L</th>
<th>L+1</th>
<th>L+2</th>
<th>L+3</th>
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<tr>
<td>HLB1</td>
<td>-8.19</td>
<td>-7.96</td>
<td>-6.36</td>
<td>-6.33</td>
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<td>-0.63</td>
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<td>-7.62</td>
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<td>-6.20</td>
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<td>0.19</td>
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<td>-1.12</td>
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<td>-1.20</td>
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**TD-DFT.** The inspection of the vertical electronic excitations between the various occupied and virtual energy levels of the studied chromophores as computed by the TD-DFT method reveals a fair agreement between computation and the experimentally observed absorption spectra (see Figure 2a and 2b). The various vertical Frank-Condon electronic excitations were computed by the TD-DFT formalism in order to comprehend the nature of electronic transitions responsible for appearance of the absorption bands in
Table 5. TD-DFT computed (CAM-B3LYP, 6-31+g(d)) representative intense vertical excitations ($\lambda_{\text{calcd}}$), associated oscillator strengths ($f$) and the experimentally observed band positions ($\lambda_{\text{obs}}$) for MS 1–8 in DCM.

<table>
<thead>
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<th>Compound</th>
<th>Transition (symmetry)</th>
<th>$\lambda_{\text{calcd}}$ ($f$) (nm)</th>
<th>$\lambda_{\text{obs}}$ (nm)</th>
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</thead>
<tbody>
<tr>
<td>MS 1</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
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<td>396</td>
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<tr>
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<td>282 (0.220)</td>
<td>335</td>
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<td></td>
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<td>292</td>
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<td></td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO+2($A_u$)</td>
<td>233 (0.274)</td>
<td>245</td>
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<tr>
<td>MS 2</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>386 (2.600)</td>
<td>399</td>
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<tr>
<td></td>
<td>HOMO($A_u$)$\rightarrow$LUMO+1($A_g$)</td>
<td>281 (0.200)</td>
<td>285</td>
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<tr>
<td></td>
<td>HOMO–4($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>272 (0.547)</td>
<td>250</td>
</tr>
<tr>
<td>MS 3</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>387 (2.568)</td>
<td>414</td>
</tr>
<tr>
<td></td>
<td>HOMO($A_u$)$\rightarrow$LUMO+1($A_g$)</td>
<td>280 (0.182)</td>
<td>275</td>
</tr>
<tr>
<td></td>
<td>HOMO–4($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>272 (0.560)</td>
<td>257</td>
</tr>
<tr>
<td>MS 4</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>395 (4.208)</td>
<td>413</td>
</tr>
<tr>
<td></td>
<td>HOMO($A_u$)$\rightarrow$LUMO+1($A_g$)</td>
<td>280 (0.182)</td>
<td>275</td>
</tr>
<tr>
<td></td>
<td>HOMO–3($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>311 (0.194)</td>
<td>323</td>
</tr>
<tr>
<td>MS 5</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>412 (4.229)</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td>HOMO($A_u$)$\rightarrow$LUMO+1($A_g$)</td>
<td>315 (0.197)</td>
<td>322</td>
</tr>
<tr>
<td>MS 6</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>413 (4.037)</td>
<td>442</td>
</tr>
<tr>
<td></td>
<td>HOMO($A_u$)$\rightarrow$LUMO+1($A_g$)</td>
<td>318 (0.200)</td>
<td>315</td>
</tr>
<tr>
<td>MS 7</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>414 (3.903)</td>
<td>435</td>
</tr>
<tr>
<td></td>
<td>HOMO($A_u$)$\rightarrow$LUMO+1($A_g$)</td>
<td>300 (0.173)</td>
<td>314</td>
</tr>
<tr>
<td></td>
<td>HOMO–7($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>277 (0.393)</td>
<td>314</td>
</tr>
<tr>
<td>MS 8</td>
<td>HOMO–1($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>428 (4.058)</td>
<td>448</td>
</tr>
<tr>
<td></td>
<td>HOMO($A_u$)$\rightarrow$LUMO+1($A_g$)</td>
<td>293 (0.159)</td>
<td>314</td>
</tr>
<tr>
<td></td>
<td>HOMO–7($A_g$)$\rightarrow$LUMO($A_u$)</td>
<td>281 (0.544)</td>
<td></td>
</tr>
</tbody>
</table>
the relevant electronic spectra. Some representative excited states for MS 1–8 are presented in Table 5.

The computed vertical excitations for MS 1–8 in DCM are shown in Figures 2a and 2b. An initial attempt to compute the excited states (TD-DFT) using the B3LYP hybrid functional had resulted in large overestimation of the absorption bands, mostly for the OPV analogues. In particular, the well-celebrated TD-DFT method is often known to produce flawed results in case of computation on the excited states of molecules with extended π–systems and those which involve a charge transfer character.26 This method (TD–DFT) is also known to be sensitive to the functional to gain the correct long-range 1/R dependence on the donor–acceptor distance in the π–expanded systems.26 The Configuration Interaction Singles (CIS) is a promising method to compute the excited states of such systems but our attempts to calculate the absorption spectra of the present OPV chromophores at this level could not improve the situation. This prompted us to use the recently developed coulomb–attenuated long-range corrected version of B3LYP i.e. CAM–B3LYP hybrid functional which indeed turned out to be very promising as this functional recovers the long-range 1/R behavior.27

The lowest energy intense absorption band in all the cases are due to the involvement of two excited states viz. HOMO–1→LUMO and HOMO→LUMO+1 excitations with high oscillator strength (f > 1) indicating a π→π* charge transfer (ICT) from the donor based molecular orbitals to the pyridine (acceptor) centered molecular orbitals. The HOMO(A_u)→LUMO(A_u) excitation in all the studied systems is symmetrically forbidden and does not contribute to the electronic absorption spectra in the relevant bipyridine dyads. The scenario of the computed electronic excitations thereby essentially points about the ‘push-pull’ architecture of the pertinent systems. Unfortunately, ~15 nm bathochromic shift of the ICT absorption maximum of MS 3 in comparison with MS 2 could not be reproduced through our computational set-up. However, an ~18 nm red-shift of the ICT absorption maximum for MS 6 has been computed as compared to MS 4, very similar to the experimentally observed ~30 nm bathochromic shift upon identical alteration of the donor position (see Table 3). Alteration of the substitution pattern from MS 4 to MS 6 causes more destabilization of the HOMOs as compared to the LUMOs resulting in attenuation of the HOMO–LUMO gap in MS 6 as compared to that in MS 4.
Figure 5. Pictorial representation of the alteration of energies of HOMOs and LUMOs while changing the substitution pattern from MS 4 to MS 6.

(Figure 5). However, the experimentally observed ~7 nm hypsochromic shift of the ICT band maximum upon increment of the number of alkoxy donors from MS 6 to MS 7 could not be reproduced.

● 4.2.6. Thermal stability
Thermal durability is one of the most significant and essential parameters for the custom-tailored applications of the bench-top synthesized compounds. The thermal decay/weight loss of the compounds MS 1–8 were examined by heating the solid samples in an analyzer under a flow of nitrogen. The thermal weight loss behavior of the chromophores MS 3, MS 5, MS 6–8 are shown in Figure 6 which depicts very high thermal stability of the relevant ‘push–pull’ chromophores. The 10% weight loss temperature (Td₁₀) for these chromophores is evidently high (~ 350 ºC) as shown in Figure 6. No significant weight loss occurs even up to 250 ºC. However, the Td₁₀ value for the compounds MS 1–2 and MS 4 are found to be relatively low (ca. 150 ºC).

● 4.3. SUMMARY AND CONCLUSION
In summary, a series of 4,4’–π–conjugated–2,2’–bipyridine dyads having a D–π–A–A–π–D architecture were synthesized wherein the 2,2’–bipyridine heterocycle acts as the central acceptor core to join the donor termini through olefinic spacers. The photophysi-
-cal properties (absorption and emission) of the synthesized chromophores are governed by the intramolecular charge separation from the donor end-capping functionalities to the pyridine acceptor heterocycle. This observation is in line with the photophysics of previously reported related dyes. The emitting state of the fluorophores is substantially more polar than the ground electronic state which is affirmed by the large solvent sensitive photoluminescent behavior of the synthesized compounds. The absorptive and emissive nature of the present chromophores are enormously dependent on the conjugation backbone i.e. the nature, position and number of donor functionalities, the parameters which act as the function of their photophysical outcome. The computational analyses of the absorption properties of the synthesized chromophores clearly depicts an alteration of the various occupied and virtual energy levels with the structure of the synthesized chromophores and is in fair agreement with the variation trend of the experimentally observed absorption spectra.

In this work, we have demonstrated optical properties of the 4,4′–π–conjugated–2,2′–bipyridine dyes which are fabricated with hetero-donor functionalities. We have shown how simple modification of the π–skeleton of these dyes modulates their fluorescence behavior. For example, among the eight dye stuffs described in this chapter, the compound, MS 5 fluoresce even in the condensed phase which is one of the pre-requirements for possible application in light emitting devices. Thus, changing the amino donor from open chain dibutylamino in MS 4 to the cyclic pyrrolidine donor in MS 5...
results in this differing photophysical behavior. Although, the 4,4′-π–conjugated–2,2′–bipyridine derivatives have been extensively studied in terms of devising nonlinear optical and solar energy harvesting materials, our systematic study on the photophysical properties of the hetero-donor systems in comparison with the parent chromophores bearing alike donor functionalities approaches a structure-function relationship which would be useful for choosing the proper material for practical applications. Accordingly, the findings of the present study in conjunction with the photophysics of the previously reported parent dye molecules construct a library of such systems in which, the present investigation finds some notable differences in the fluorescence responses compared to the parent molecules functionalized with only one kind of donor sub-chromophores. The present work reveals that the coexistence of both the alkoxy and amino functionalities in the same phenyl ring modulates the emitting state of MS 2 and MS 4 which exhibit considerable bathochromic shifted fluorescence with respect to the reported chromophores having either alkoxy (N945L, TM 6) or amino (HLB 1-2) donor groups. Furthermore, moving the alkoxy donors from ring–B (MS 4) to ring–A (MS 6) results in a large bathochromic shift of the absorption wavelength presumably due to the enhanced participation of the alkoxy groups in the charge transfer process when placed in ring-A than in ring-B. The introduction of additional alkoxy donor functionalities has not induced further bathochromic shift of the absorption maxima.

● 4.4. EXPERIMENTAL SECTION
● 4.4.1. Materials and methods
All the reactions were performed under either ultra high pure nitrogen or argon atmosphere unless mentioned elsewhere. The commercially procured chemicals were used as received. Triethylphosphite was distilled prior to use. THF, diethyl ether was freshly distilled over Na / Benzophenone under nitrogen until a deep purple color persists and used either immediately (THF) or stored over sodium wire in the dark (ether). Triethylamine, diisopropylamine were distilled thrice over calcium hydride under nitrogen and stored over KOH/NaOH pellets in a CaCl₂ desiccator. Aniline was distilled over KOH and used immediately. All the deuteriated NMR solvents were purchased from Acros Organics and used as received. Column chromatography was performed with silica gel (100–200 mesh) (SRL, India) unless mentioned. All the solvents used for the
chromatographic purifications were distilled prior to use. NMR spectra (\(^1\)H and \(^{13}\)C) were recorded by Bruker AV–400 MHz spectrometer using tetramethylsilane (TMS) as internal standard in case of CDCl\(_3\) solvent. Signal multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Elemental analyses were performed by FLASH EA series 1112 CHNS analyzer. The infrared spectra were recorded on a JASCO–5300 FT-IR spectrophotometer. Thermogravimetric analyses were carried out on a STA 409 PC analyzer under the flow of nitrogen. HRMS (MALDI-TOF/TOF) spectra of MS 4–8 were recorded in \(\alpha\)-cyanocinnamic acid matrix. Cary 100 Bio UV-visible spectrophotometer and Shimadzu UV–3600 spectrophotometer was used to record the electronic absorption spectra. The emission spectra were recorded on a Fluoromax–4 (Jobin Yvon) spectrofluorometer and corrected for the instrumental response. Dilute solutions with OD \(\approx 0.05\) at the excitation wavelength were used for the quantum yield measurements (error limit \(\pm 10\%\)). Optically matched solutions of the sample and the reference were measured under the same operating condition and instrumental settings.

4.4.2. Synthesis and characterization data

\(N,N\)–dibutylaniline (4a). A mixture of aniline (19 mL, 200 mmol), 1–bromo butane (65 mL, 600 mmol) and Na\(_2\)CO\(_3\) (84 g, 800 mmol) in 100 mL of 90:10 v/v DMF/NMP was heated at 120 °C for 24 h. The reaction mixture was then cooled to room temperature and filtered to remove the insoluble material. The precipitate was washed with ethyl acetate and the combined filtrate was evaporated to dryness. Water was then added and the aqueous phase was extracted with ethyl acetate. After a silica gel filtration using hexane as the mobile phase, the pure compound was obtained as a pale yellow liquid. Yield: 35.3 g (86%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.25–7.21 (unresolved, 2H), 6.68 (unresolved, 3H), 3.29 (t, 4H), 1.58 (unresolved, 4H), 1.41–1.35 (m, 4H), 1.00 (t, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 129.2, 115.1, 111.7, 50.8, 29.4, 20.4, 14.0.

LC–MS (positive mode): \(m/z\) 206 (M+H\(^+\)).

Anal. calcd. for C\(_{14}\)H\(_{23}\)N: C, 81.89; H, 11.29; N, 6.82. Found: C, 81.83; H, 11.33; N, 6.84.
N,N-dibutyl-2,5-dimethoxyaniline (4b). This compound was synthesized using the same procedure as described for compound 4a. 2,5-dimethoxy aniline (3b, 30.6 g, 200 mmol) was used instead of aniline (3a) and the reaction time was 72 h at 120 °C. The black crude liquid was subjected to silica gel filtration using hexane as the eluent to obtain the pure product 4b as a light sensitive pale yellow liquid.

Yield: 38.7 g (73%).

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 6.76 (d, J = 8 \text{ Hz, } 1H), 6.54 (d, \spa{4}J_{HH} = 4 \text{ Hz, } 1H), 6.46–6.43 (dd, J = 8 \text{ Hz, } \spa{4}J_{HH} = 4 \text{ Hz, } 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.08 (t, 4H), 1.45 (p, 4H), 1.28 (sextet, 4H), 0.88 (t, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 153.9, 147.9, 141.3, 112.8, 108.7, 104.7, 56.2, 55.5, 52.4, 26.9, 20.5, 14.1.

LC–MS (positive mode): \(m/z\) 266 (M+H)

Anal. calcd. for C\(_{16}\)H\(_{27}\)NO\(_2\): C, 72.41; H, 10.25; N, 5.28. Found: C, 72.47; H, 10.11; N, 5.32.

4-(dibutylamino)benzaldehyde (5a). POCl\(_3\) (5.5 mL, 60 mmol) was slowly added to a DMF (20 mL, excess) solution of N,N–dibutyl aniline (4a, 10.25 g, 50 mmol) with cooling in an ice bath under an inert atmosphere. The resulting orange–red viscous liquid was then stirred at this temperature for 15 min, slowly warmed up to room temperature and then heated at 90–95 °C for 7 h. The dark reaction mixture was then cooled in an ice bath and carefully quenched with water, followed by neutralization with aqueous Na\(_2\)CO\(_3\) solution. The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water, brine, dried (anhydrous Na\(_2\)SO\(_4\)) and evaporated. Chromatographic purification of the crude mixture in a silica gel (100–200 mesh) column eluting with EtOAc/Hexane 15:85 v/v gave the product 5a as a yellow viscous liquid.

Yield: 11.16 g (95%).

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 9.69 (s, 1H), 7.69 (d, J = 8 \text{ Hz, } 2H), 6.64 (d, J = 8 \text{ Hz, } 2H), 3.35 (t, 4H), 1.60 (p, 4H), 1.36 (hextet, 4H), 0.97 (t, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 189.9, 152.6, 132.2, 124.5, 110.7, 50.8, 29.3, 20.3, 20.25, 13.9.

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IR (neat, cm$^{-1}$): $\nu_{\text{max}}$ 1680 (>C=O).
LC–MS (positive mode): $m/z$ 234 [M+H]$^+$. 
Anal. calcd. for C$_{15}$H$_{23}$NO: C, 77.21; H, 9.93; N, 6.00. Found: C, 77.27; H, 9.84; N, 6.12.

4-(dibutylamino)-2,5-dimethoxybenzaldehyde (5b). This compound was synthesized using the same procedure as described for 5a. N,N-dibutyl-2,5-dimethoxyaniline (2b, 13.25 g, 50 mmol) was used instead of N,N-dibutyl aniline (2a). Reaction time at 90–95 °C: 4 h. The product 5b was isolated as an orange–yellow viscous liquid after silica gel (100–200 mesh) filtration of the crude with EtOAc/Hexane 20:80 v/v as the mobile phase. Yield: 12.60 g (86%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.20 (s, 1H), 7.25 (s, 1H), 6.27 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.30 (t, 4H), 1.55 (p, 4H), 1.31 (heptet, 4H), 0.90 (t, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 187.3, 158.6, 147.9, 145.3, 115.9, 110.1, 100.6, 55.98, 55.90, 52.2, 29.8, 20.4, 14.0.
IR (neat, cm$^{-1}$): $\nu_{\text{max}}$ 1660 (>C=O).
LC–MS (positive mode): $m/z$ 294 [M+H]$^+$. 
Anal. calcd. for C$_{17}$H$_{27}$NO$_3$: C, 69.59; H, 9.28; N, 4.77. Found: C, 69.51; H, 9.33; N, 4.70.

1-phenylpyrrolidine (6a). A mixture of aniline (4.6 mL, 50 mmol), 1,4-dibromobutane (6.5 mL, 55 mmol) and K$_2$CO$_3$ (28 g, 200 mmol) in 90:10 v/v DMF/N-methylpyrrolidinone (NMP) was heated at 120 °C for 24 h after which it was cooled to room temperature and filtered. The precipitated solid was washed with ethyl acetate and the combined filtrate was evaporated to dryness. Water was then added and the aqueous phase was extracted with ethyl acetate. The crude product was purified on short silica gel column eluting with EtOAc/Hexane 1:99 v/v to yield the pure product 6a as a light sensitive yellow liquid. Yield: 4.7 g (62%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29–7.25 (unresolved, 2H), 6.70–6.61 (m, 3H), 3.32 (unresolved, 4H), 2.04 (unresolved, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 148.2, 129.2, 115.6, 111.8, 47.7, 25.5.
LC–MS (positive mode): $m/z$ 148 (M+H)$^+$.  


1–(2,5–dimethoxyphenyl)pyrrolidine (6b). This compound was prepared using the same procedure as described for the synthesis of compound 6a.  

7.6 g (50 mmol) 2,5–dimethoxy aniline was used instead of aniline and the reaction mixture was heated at 120 °C for 48 h. Silica gel filtration using EtOAc/Hexane 5:95 v/v as the mobile phase afforded the pure compound 6b as a yellow light sensitive liquid. Yield: 7.9 g (76%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.78 (d, $J=8$ Hz, 1H), 6.38 (d, $^4J_{HH}=4$ Hz, 1H), 6.34–6.31 (dd, $J=8$ Hz, $^4J_{HH}=4$ Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 33.2 (unresolved, 4H), 19.4 (unresolved, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.5, 144.8, 141.1, 113.0, 103.1, 101.6, 56.6, 55.5, 50.4, 24.5.

LC–MS (positive mode): $m/z$ 208 (M+H)$^+$.  

Anal. calcd. for C$_{12}$H$_{17}$NO$_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.41; H, 8.23; N, 6.73.

4–(pyrrolidin–1–yl)benzaldehyde (7a). This compound was synthesized using the same procedure as described for 5a.  

1–phenylpyrrolidine (6a, 7.35 g, 50 mmol) was used instead of $N,N$–dibutyl aniline (4a). Reaction time at 90–95 °C: 6–7 h. Column chromatographic (silica gel, 100–200 mesh) purification of the crude product using EtOAc/Hexane 20:80 v/v as the eluent afforded the desired product 7a as a white crystalline solid. Yield: 7.26 g (83%). Mp: 81–83 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.72 (s, 1H), 7.73 (d, $J=8$ Hz, 2H), 6.57 (d, $J=8$ Hz, 2H), 3.41–3.37 (m, 4H), 2.07–2.04 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 190.2, 152.0, 132.1, 124.9, 111.2, 47.7, 25.4.

IR (KBr, cm$^{-1}$): $\nu_{max}$ 1674 (>C=O).

LC–MS (positive mode): $m/z$ 176 [M+H]$^+$.  

Anal. calcd. for C$_{11}$H$_{13}$NO: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.45; H, 7.39; N, 8.07.
2,5-dimethoxy-4-(pyrrolidin-1-yl)benzaldehyde (7b). This compound was synthesized using the same procedure as described for 5a. 1-(2,5-dimethoxyphenyl)pyrrolidine (6b, 10.35 g, 50 mmol) was used instead of \( N,N \)-dibutyl aniline (4a). Reaction time at 90–95 ºC: 7–8 h. The crude product was purified by silica gel (100–200 mesh) column eluting with EtOAc/Hexane 20:80 v/v as the mobile phase to obtain the pure aldehyde 7b as a light sensitive cream colored solid. Yield: 10.34 g (88%). Mp: 120–121 ºC.

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta 10.13 (s, 1H), 7.23 (s, 1H), 6.00 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 3.55 (unresolved, 4H), 1.93 (unresolved, 4H). \]

\[ \text{C NMR (100 MHz, CDCl}_3\text{): } \delta 186.7, 159.5, 146.7, 142.9, 113.8, 110.1, 96.2, 56.4, 55.8, 50.7, 25.5. \]

\[ \text{IR (KBr, cm}^{-1}\text{): } \nu_{\text{max}} 1639 (>\text{C}=\text{O}). \]

LC–MS (positive mode): \( m/z \) 236 [M+H]^+.

Anal. calcd. for C_{13}H_{17}NO_3: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.28; H, 7.25; N, 6.11.

\( (E)-4-(4-(\text{pyrrolidin-1-yl})\text{styryl})\text{bromobenzene (10a).} \) Solid potassium \( t \)-butoxide (1.68 g, 15 mmol) was added at once to an ice–cooled THF solution (30 mL) containing 3.68 g of phosphonate 8 (12 mmol) and 1.75 g of aldehyde 7a (10 mmol) under an inert atmosphere. The resulting slurry was warmed up to room temperature and stirred for 1 h before the reaction was quenched with water. The precipitated yellow solid was collected by filtration, washed several times with water and dried in air. It was re–dissolved in dichloromethane (ca. 600 mL) and the solvent was rotavaporated to ca. 15 mL and filtered to obtain the pure product 10a as a yellow solid. Yield: 2.85 g (87%). Mp: more than 200 ºC.

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta 7.43 (d, J = 8 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 7.03 (d, J = 16 Hz, 1H), 6.81 (d, J = 16 Hz, 1H), 6.55 (d, J = 8 Hz, 2H), 3.33 (unresolved, 4H), 2.02 (unresolved, 4H). \]

\[ \text{C NMR was not possible because of low solubility.} \]

LC–MS (positive mode): \( m/z \) 328 (M)^+, 330 (M+2H)^+. 

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Anal. calcd. for C_{18}H_{18}BrN: C, 65.86; H, 5.53; N, 4.27. Found: C, 65.69; H, 5.48; N, 4.30.

(E)-4-(4-(dibutylamino)-2,5–dimethoxystyryl)bromobenzene (11a). Under nitrogen, solid potassium t–butoxide (1.68 g, 15 mmol) was added at once to a THF solution (30 mL) containing 3.68 g of phosphonate 8 (12 mmol) and 2.93 g of aldehyde 5b (10 mmol) pre–cooled at 0 ºC. The ice bath was removed and the reaction mixture was allowed to stir at room temperature for 60 min. It was subsequently quenched with water and then extracted with dichloromethane. The combined organic phase was washed with brine, dried over anhydrous Na_{2}SO_{4} and evaporated to dryness. Purification of the crude product through column chromatography (silica gel, 100–200 mesh) using EtOAc/Hexane 5:95 v/v as the eluent afforded the product 11a as a dark yellow solid. Yield: 4.06 g (91%). Mp: 76–78 ºC.

\[ \text{1H NMR (400 MHz, CDCl}_3): \delta 7.46–7.37 (m, 5H), 7.06 (s, 1H), 6.89 (d, J = 16 Hz, 1H), 6.50 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.16 (t, 4H), 1.51 (p, 4H), 1.33 (m, 4H), 0.90 (t, 6H). \]

\[ \text{13C NMR (100 MHz, CDCl}_3): \delta 151.8, 147.4, 141.4, 137.4, 131.6, 127.7, 125.0, 124.1, 120.4, 118.4, 110.3, 105.2, 52.3, 29.3, 20.6, 14.1. \]

LC–MS (positive mode): m/z 446 (M)^+, 448 (M+2H)^+.

Anal. calcd. for C_{24}H_{32}BrNO_{2}: C, 64.57; H, 7.23; N, 3.14. Found: C, 64.43; H, 7.16; N, 3.16.

(E)-4-(2,5–dimethoxy–4–(pyrrolidin–1–yl)styryl)bromobenzene (12a). This compound was prepared using the same procedure as described for 11a using 3.68 g of phosphonate 8 (12 mmol), 2.35 g of aldehyde 7b (10 mmol) and 1.68 g of potassium t–butoxide (15 mmol) in 30 mL of THF. Column chromatographic purification on silica gel (100–200 mesh) using EtOAc/Hexane 20:80 v/v as the mobile phase afforded the product 12a as fluorescent yellow needles. Yield: 3.65 g (94%). Mp: 128–130 ºC.
\[ \text{Chapter 4} \]

D–\(\pi\)–A–\(\pi\)–D Prototype 2,2’–Bipyridine…

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.45–36 (m, 5H), 7.07 (s, 1H), 6.85 (d, \(J = 16\) Hz, 1H), 6.29 (s, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.41 (unresolved, 4H), 1.96 (unresolved, 4H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 152.5, 144.1, 141.1, 137.7, 131.6, 127.6, 124.2, 123.5, 120.0, 115.3, 99.6, 56.9, 56.4, 50.5, 25.1.

LC–MS (positive mode): \(m/z \) 388 (M), 390 (M+2H).

Anal. calcd. for C\(_{20}\)H\(_{22}\)BrNO\(_2\): C, 61.86; H, 5.71; N, 3.61. Found: C, 62.01; H, 5.64; N, 3.55.

\((E)\)–2,5–dibutoxy–4–(4–(dibutylamino)styryl)bromobenzene (13a). This compound was prepared using the same procedure as described for 11a using 2.3 g of phosphonate 7 (5 mmol), 1.1 g of aldehyde 5a (4.8 mmol) and 0.7 g of potassium \(t\)–butoxide (6 mmol) in 25 mL of THF. The product 13a was isolated as a fluorescent yellow solid after column chromatography on silica gel (100–200 mesh) using EtOAc/Hexane 5:95 v/v as the mobile phase. Yield: 2.34 g (92%). Mp: 84–86 ºC.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.39 (d, \(J = 8\) Hz, 2H), 7.16 (d, \(J = 16\) Hz, 1H), 7.12 (s, 1H), 7.06 (s, 1H), 7.02 (d, \(J = 16\) Hz, 1H), 6.54 (d, \(J = 8\) Hz, 2H), 4.05 (t, 2H), 3.95 (t, 2H), 3.30 (t, 4H), 1.82 (p, 4H), 1.63–1.52 (m, 8H), 1.36 (t, 4H), 1.03–0.96 (m, 12H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta \) 150.7, 149.9, 147.9, 129.6, 127.8, 124.9, 117.8, 111.6, 111.2, 110.3, 70.0, 69.3, 50.8, 31.5, 29.5, 20.4, 19.4, 14.0.

LC–MS (positive mode): \(m/z \) 531 (M), 533 (M+2H).

Anal. calcd. for C\(_{30}\)H\(_{44}\)BrNO\(_2\): C, 67.91; H, 8.36; N, 2.64. Found: C, 68.02; H, 8.25; N, 2.69.

\((E)\)–2,5–dibutoxy–4–(4–(dibutylamino)–2,5–dimethoxystyryl)bromobenzene (14a). This compound was prepared using the same procedure as described for 11a using 2.3 g of phosphonate 7 (5 mmol), 1.4 g of aldehyde 5b (4.8 mmol) and 0.7 g of potassium \(t\)–butoxide (6 mmol) in 25 mL of THF. The product 14a was isolated as a yellow solid after chromatographic purification on silica gel stationary phase (100–200 mesh) using EtOAc/Hexane 5:95 v/v as the mobile phase. Yield: 2.61 g (92%). Mp: 58–60 ºC.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) 7.41 (d, \(J = 16\) Hz, 1H), 7.26 (d, \(J = 16\) Hz, 1H), 7.15 (s, 1H), 7.10 (s, 1H), 7.07 (s, 1H), 6.51 (s, 1H), 4.05 (t, 2H), 3.96 (t, 2H), 3.86–3.85 (m, 6H),
3.15 (t, 4H), 1.85–1.78 (m, 4H), 1.60–1.43 (m, 8H), 1.29 (m, 4H), 0.99 (t, 6H), 0.91 (t, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 151.7, 150.9, 149.9, 147.6, 141.1, 127.8, 123.9, 120.8, 119.4, 117.9, 111.7, 110.9, 110.5, 105.4, 70.0, 69.3, 56.5, 56.3, 52.4, 31.5, 29.4, 20.6, 19.4, 19.3, 14.0, 13.9.

LC–MS (positive mode): $m/z$ 590 (M)$^+$, 592 (M+2H)$^+$.

Anal. calcd. for C$_{32}$H$_{48}$BrNO$_4$: C, 65.07; H, 8.19; N, 2.37. Found: C, 65.10; H, 8.08; N, 2.43.

($E$)–2,5–dibutoxy–4–(2,5–dimethoxy–4–(pyrrolidin–1–yl)styryl)bromobenzene (15a).

This compound was synthesized by the same procedure as described for 11a using 2.3 g of phosphonate 7 (5 mmol), 1.1 g of aldehyde 7b (4.8 mmol) and 0.7 g of potassium t–butoxide (6 mmol) in 25 mL of THF. Chromatographic purification using silica gel stationary phase (100–200 mesh) and EtOAc/Hexane 10:90 v/v as the mobile phase afforded the product 15a as a fluorescent yellow solid. Yield: 2.25 g (88%). Mp: 116–118 ºC.

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.40 (d, $J$ = 16 Hz, 1H), 7.20 (d, $J$ = 16 Hz, 1H), 7.15 (s, 1H), 7.10 (s, 1H), 7.06 (s, 1H), 6.30 (s, 1H), 4.05 (t, 2H), 3.96 (t, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.41 (unresolved, 4H), 1.95 (unresolved, 4H), 1.81 (p, 4H), 1.56 (m, 4H), 1.00 (t, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 152.4, 150.8, 149.9, 144.2, 140.8, 128.0, 124.0, 119.2, 117.9, 116.3, 111.4, 110.8, 110.4, 99.8, 70.0, 69.4, 56.8, 56.5, 50.5, 31.5, 25.1, 19.4, 19.3, 14.0.

LC–MS (positive mode): $m/z$ 532 (M)$^+$, 534 (M+2H)$^+$.

Anal. calcd. for C$_{28}$H$_{38}$BrNO$_4$: C, 63.15; H, 7.19; N, 2.63. Found: C, 63.21; H, 7.22; N, 2.68.

($E$)–4–(4–(pyrrolidin–1–yl)styryl)benzaldehyde (10b). A solution of bromostilbene 10a (0.98 g, 3 mmol) in 110 mL of THF was cooled to –40 ºC and then 2.2 mL of 1.6 M nBuLi (3.6 mmol) was added dropwise. The heterogeneous mixture was stirred at this
temperature for 60 min, 0.4 mL of dry DMF (5 mmol) was subsequently added followed by stirring at this temperature for additional 60 min. The cooled reaction mixture was then slowly warmed up to room temperature, quenched with saturated ammonium chloride solution and extracted with dichloromethane. The organic layer was washed twice with water, then with brine, dried (Na$_2$SO$_4$) and evaporated to dryness. The crude product was purified by column chromatography on silica gel (100–200 mesh) using dichloromethane as the mobile phase to obtain the pure aldehyde 10b as an orange yellow solid. Yield: 0.66 g (80%). Mp: more than 200 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.96 (s, 1H), 7.83 (d, $J = 8$ Hz, 2H), 7.60 (d, $J = 8$ Hz, 2H), 7.43 (d, $J = 8$ Hz, 2H), 7.22 (d, $J = 16$ Hz, 1H), 6.92 (d, $J = 16$ Hz, 1H), 6.57 (d, $J = 8$ Hz, 2H), 3.33 (unresolved, 4H), 1.58 (unresolved, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.7, 148.1, 144.8, 134.3, 132.9, 130.3, 129.4, 128.4, 126.2, 121.9, 111.8, 47.6, 25.5.

IR (KBr, cm$^{-1}$): $\nu_{\text{max}}$ 1691 (>C=O).

LC–MS (positive mode): $m/z$ 278 (M+H)$^+$. Anal. calcd. for C$_{19}$H$_{19}$NO: C, 82.28; H, 6.90; N, 5.05. C, 88.23; H, 6.88; N, 5.12.

$(E)$–4–(4–(dibutylamino)–2,5–dimethoxystyryl)benzaldehyde (11b). This compound was synthesized by the same procedure as described for aldehyde 10b. Reactant amount is as follows: bromostilbene 11a (1.34 g, 3 mmol), 1.6 M nBuLi (2.2 mL, 3.6 mmol), DMF (0.4 mL, 5 mmol), 20 mL of THF was used instead. Chromatographic purification using silica gel stationary phase (100–200 mesh) and EtOAc/Hexane 10:90 v/v mobile phase rendered the aldehyde 11b as a vermilion red gummy mass. Yield: 0.81 g (68%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.97 (s, 1H), 7.84 (d, $J = 8$ Hz, 2H), 7.60 (d, $J = 8$ Hz, 2H), 7.61 (d, $J = 16$ Hz, 1H), 7.09 (s, 1H), 7.01 (d, $J = 16$ Hz, 1H), 6.49 (s, 1H), 3.87 (unresolved, 6H), 3.18 (t, 4H), 1.52–1.47 (p, 4H), 1.33–1.26 (m, 4H), 0.91 (t, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.7, 152.3, 147.8, 144.8, 142.2, 134.6, 130.2, 127.0, 126.5, 124.6, 117.6, 110.5, 104.6, 56.40, 56.35, 52.2, 29.4, 20.5, 14.1.
IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) 1695 (\(>\text{C}=\text{O}\)).

LC–MS (positive mode): \(m/z\) 396 (M+H).\(^+\).

Anal. calcd. for C\(_{23}\)H\(_{33}\)NO\(_3\): C, 75.91; H, 8.41; N, 3.54. Found: C, 76.09; H, 8.35; N, 3.58.

\((E)-4-(2,5-\text{dimethoxy}-4-(\text{pyrrolidin-1-yl})\text{styryl})\text{benzaldehyde} \quad (12b)\). This compound was synthesized by the same procedure as described for aldehyde 10b using bromostilbene 12a (1.16 g, 3 mmol), 1.6 M \(n\)BuLi (2.2 mL, 3.6 mmol), DMF (0.4 mL, 5 mmol) in 20 mL of THF. Purification of the crude product by column chromatography using silica gel (100–200 mesh) and EtOAc/Hexane 10:90 v/v mobile phase afforded the aldehyde 12b as a vermillion orange solid. Yield: 0.71 g (70%). Mp: 120–122 ºC.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.96 (s, 1H), 7.82 (d, \(J = 8\ \text{Hz}, 2\)H), 7.64–7.59 (m, 3H), 7.09 (s, 1H), 6.95 (d, \(J = 16\ \text{Hz}, 1\)H), 6.26 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.44 (unresolved, 4H), 1.96 (unresolved, 4H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 191.7, 153.1, 145.1, 143.9, 141.8, 134.3, 130.3, 127.2, 126.3, 123.0, 114.6, 111.0, 99.1, 57.0, 56.3, 50.5, 25.2.

IR (KBr, cm\(^{-1}\)): \(\nu_{\text{max}}\) 1689 (\(>\text{C}=\text{O}\)).

LC–MS (positive mode): \(m/z\) 338 (M+H).\(^+\).

Anal. calcd. for C\(_{21}\)H\(_{23}\)NO\(_3\): C, 74.75; H, 6.87; N, 4.15. Found: C, 74.62; H, 6.84; N, 4.13.

\((E)-2,5-\text{dibutoxy}-4-(4-(\text{dibutylamino})\text{styryl})\text{benzaldehyde} \quad (13b)\). This compound was synthesized by the same procedure as described for aldehyde 10b using bromostilbene 13a (1.6 g, 3 mmol), 1.6 M \(n\)BuLi (2.2 mL, 3.6 mmol), DMF (0.4 mL, 5 mmol) in 20 mL of THF. Chromatographic purification of the crude product on silica gel (100–200 mesh) using EtOAc/Hexane 5:95 v/v as the eluent afforded the aldehyde 13b as a thick red gum. Yield: 0.82 g (57%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.44 (s, 1H), 7.43 (d, \(J = 8\ \text{Hz}, 2\)H), 7.31 (s, 1H), 7.23
(d, J = 16 Hz, 1H), 7.16 (s, 1H), 6.65 (d, J = 8 Hz, 2H), 4.13 (t, 2H), 4.03 (t, 2H), 3.32 (t, 4H), 1.86–1.83 (m, 4H), 1.59–1.53 (m, 8H), 1.41–1.37 (m, 4H), 1.04–0.96 (m, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.0, 156.5, 150.3, 148.3, 135.8, 132.7, 128.4, 124.4, 123.2, 117.4, 111.6, 110.0, 109.6, 68.9, 68.7, 50.8, 31.4, 29.5, 20.4, 19.4, 14.0.

IR (KBr, cm$^{-1}$): $\nu_{max}$ 1672 (>C=O).

LC–MS (positive mode): $m/z$ 481 (M+H)$^+$.  

Anal. calcd. for C$_{31}$H$_{45}$NO$_3$: C, 77.62; H, 9.46; N, 2.92. Found: C, 77.51; H, 9.42; N, 3.00.

(E)-2,5-dibutoxy-4-(4-(dibutylamino)-2,5-dimethoxy-4-styryl)benzaldehyde (14b). This compound was synthesized by the same procedure as described for aldehyde 10b using bromostilbene 14a (1.8 g, 3 mmol), 1.6 M nBuLi (2.2 mL, 3.6 mmol), DMF (0.4 mL, 5 mmol) in 20 mL of THF. The crude product was subjected to column chromatography on silica gel (100–200 mesh) using EtOAc/Hexane 5:95 v/v as the mobile phase to afford the aldehyde 14b as a thick red gum. Yield: 0.76 g (47%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.42 (s, 1H), 7.58 (d, J = 16 Hz, 1H), 7.55 (d, J = 16 Hz, 1H), 7.30 (s, 1H), 7.19 (s, 1H), 7.12 (s, 1H), 6.50 (s, 1H), 4.12 (t, 2H), 4.02 (t, 2H), 3.86 (s, 6H), 3.18 (t, 4H), 1.83 (p, 4H), 1.58–1.48 (m, 8H), 1.31 (m, 4H), 1.00 (t, 6H), 0.91 (t, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 189.1, 156.4, 152.2, 150.5, 147.2, 141.9, 135.7, 126.9, 123.5, 120.2, 118.5, 110.6, 110.0, 109.9, 104.7, 68.8, 68.7, 56.4, 56.2, 52.2, 31.4, 31.3, 29.4, 20.5, 19.5, 19.3, 14.1, 14.0, 13.9.

IR (KBr, cm$^{-1}$): $\nu_{max}$ 1674 (>C=O).

LC–MS (positive mode): $m/z$ 541 (M+H)$^+$.  

Anal. calcd. for C$_{33}$H$_{49}$NO$_5$: C, 73.43; H, 9.15; N, 2.60. Found: C, 73.57; H, 9.09; N, 2.53.

(E)-2,5-dibutoxy-4-(2,5-dimethoxy-4-(pyrrolidin-1-yl)styryl)benzaldehyde (15b). This compound was synthesized by the same procedure as described for aldehyde 10b using bromostilbene 15a (1.6 g, 3 mmol), 1.6 M nBuLi (2.2 mL, 3.6 mmol), DMF (0.4 mL, 5 mmol) in 20 mL of THF. Purification of the crude product by silica gel (100–200
mesh) column chromatography using EtOAc/Hexane 10:90 v/v as the mobile phase afforded the aldehyde 15b as a vermillion orange solid. Yield: 0.72 g (50%). Mp: 103–105 ºC.

$^1$H NMR (400 MHz, CDCl$_3$): 10.42 (s, 1H), 7.58 (d, $J = 16$ Hz, 1H), 7.30 (d, $J = 16$ Hz, 1H), 7.29 (s, 1H), 7.19 (s, 1H), 7.12 (s, 1H), 6.27 (s, 1H), 4.42 (t, 2H), 4.43 (t, 2H), 3.88 (s, 3H), 3.82 (s, 3H), 3.43 (unresolved, 4H), 1.95 (unresolved, 4H), 1.84 (p, 4H), 1.56 (m, 4H), 0.99 (t, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.5, 153.0, 150.4, 143.9, 141.5, 136.1, 127.1, 123.3, 118.6, 115.5, 111.1, 110.0, 109.8, 99.3, 68.9, 68.8, 56.9, 56.3, 50.4, 31.4, 25.2, 19.5, 19.4, 13.9.

IR (KBr, cm$^{-1}$): $\nu_{\text{max}}$ 1670 (>C=O).

LC–MS (positive mode): $m/z$ 483 (M+H)$^+$. 

Anal. calcd. for C$_{29}$H$_{39}$NO$_5$: C, 72.32; H, 8.16; N, 2.91. C, 72.27; H, 8.19; N, 3.01.

4,4′-bis[(4-(pyrrolidin-1-yl)styryl)-2,2′-bipyridine (MS 1). Under nitrogen, solid potassium tert–butoxide (0.45 g, 4 mmol) was added at a time to a THF solution (50 mL) of the bis–phosphonate (2, 0.46 g, 1 mmol) and the aldehyde (7a, 0.39 g, 2.2 mmol) at room temperature and the resulting heterogeneous reaction mixture was stirred at this temperature for 3 h. The reaction mixture was subsequently quenched with water (25 mL), evaporated to dryness and methanol 50 mL was added to cause precipitation of the product. It was collected by filtration, washed several times with water, methanol and a small amount of ether and dried in air. It was re-dissolved in dichloromethane (ca. 500 mL) and the yellow solution was concentrated to almost 20 mL. The bright yellow precipitated material was collected by filtration and dried thoroughly. The compound MS 1 was isolated as a yellow microcrystalline solid. Yield: 0.46 g (92%). Mp (Differential Thermal Analysis, DTA): 357 ºC.

$^1$H NMR (400 MHz, CDCl$_3$): δ 8.615 (d, $J = 4$ Hz, 2H), 8.48 (s, 2H), 7.46 (d, $J = 8$ Hz, 4H), 7.41 (d, $J = 16$ Hz, 2H), 7.345 (d, $J = 4$ Hz, 2H), 6.90 (d, $J = 16$ Hz, 2H), 6.58 (d, $J = 8$ Hz, 4H), 3.35 (unresolved, 8H), 2.03 (unresolved, 8H).
\(^{13}\)C NMR was not possible because of low solubility.

LC–MS (positive mode): \(m/z\) 499 (M+H)^+.

Anal. calcd. for C\(_{34}\)H\(_{34}\)N\(_4\): C, 81.89; H, 6.87; N, 11.24. Found: C, 81.72; H, 6.81; N, 11.15.

**4,4’–bis(4–dibutylamino–2,5–dimethoxystyryl)–2,2’–bipyridine** (MS 2). Neat potassium t–butoxide (0.45 g, 4 mmol) was added at once to a mixture of the bis–phosphonate (2, 0.46 g, 1 mmol) and the aldehyde (5b, 0.64 g, 2.2 mmol) dissolved in 50 mL of THF at room temperature under an inert atmosphere and the dark colored reaction mixture thus obtained was stirred at this temperature for 3 h. It was then quenched with water (25 mL) and the product was extracted with dichloromethane. The organic layer was washed with brine, dried over anhydrous Na\(_2\)SO\(_4\) and subjected to chromatographic purification over silica gel (100–200 mesh) column using methanol/chloroform 5:95 v/v as the eluent to obtain the compound MS 2 as a dark colored thick gum. Yield: 0.66 g (90%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.635 (d, \(J = 4\) Hz, 2H), 8.48 (s, 2H), 7.75 (d, \(J = 16\) Hz, 2H), 7.435 (d, \(J = 4\) Hz, 2H), 7.09 (s, 2H), 7.05 (d, \(J = 16\) Hz, 2H), 6.50 (s, 2H), 3.88 (unresolved, 12H), 3.19 (t, 8H), 1.53–1.47 (p, 8H), 1.34–1.26 (m, 8H), 0.91 (t, 12H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\), C-type based on DEPT-135 spectrum): \(\delta\) 156.6 (C), 152.5 (C), 149.3 (CH), 147.1 (C), 146.9 (C), 142.3 (C), 128.2 (CH), 123.7 (CH), 120.3 (CH), 118.5 (CH), 117.4 (C), 111.0 (CH), 104.6 (CH), 56.3 (OMe), 52.2 (CH\(_2\)), 29.4 (CH\(_2\)), 20.5 (CH\(_2\)), 14.0 (CH\(_3\)).

LC–MS (positive mode): \(m/z\) 736 (M+H)^+.

Anal. calcd. for C\(_{46}\)H\(_{62}\)N\(_4\)O\(_4\): C, 75.17; H, 8.50; N, 7.62. Found: C, 75.23; H, 8.41; N, 7.56.

**4,4’–bis(2,5–dimethoxy–4–(pyrrolidin–1–yl)styryl)–2,2’–bipyridine** (MS 3). This compound was obtained using the same procedure as described for MS 2. The aldehyde 7b (0.52 g, 2.2 mmol) was used instead of aldehyde 5b. Column chromatographic purification (silica gel, 100–200 mesh) using methanol/chloroform 5:95 v/v as the mobile
phase resulted in the isolation of the pure compound **MS 3** as a brown microcrystalline solid. Yield: 0.56 g (91%). Mp (DTA): 250 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.605 (d, $J = 4$ Hz, 2H), 8.46 (s, 2H), 7.75 (d, $J = 16$ Hz, 2H), 7.42 (d, $J = 8$ Hz, 2H), 7.10 (s, 2H), 6.98 (d, $J = 16$ Hz, 2H), 6.27 (s, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 3.44 (unresolved, 8H), 1.95 (unresolved, 8H).

$^{13}$C NMR (100 MHz, CDCl$_3$, C-type based on DEPT-135 spectrum): $\delta$ 153.3 (C), 149.1 (CH), 147.4 (C), 143.8 (C), 141.8 (C), 128.4 (CH), 122.1 (CH), 120.2 (CH), 118.4 (CH), 114.4 (C), 111.4 (CH), 99.1 (CH), 56.9 (OMe), 56.2 (OMe), 50.5 (CH$_2$), 25.2 (CH$_2$).

LC–MS (negative mode): $m/z$ 618 (M–H$^+$).

Anal. calcd. for C$_{38}$H$_{42}$N$_4$O$_4$: C, 73.76; H, 6.84; N, 9.05. Found: C, 73.61; H, 6.78; N, 9.15.

**4,4’–bis(4–(2,5–dimethoxy–4–dibutylaminostyryl)styryl)–2,2’–bipyridine (MS 4).**

The synthesis of this compound follows the same procedure as described for **MS 2**. Aldehyde **11b** (0.86 g, 2.2 mmol) was used instead of aldehyde **5b**. The crude product was purified through column chromatography using silica gel (100–200 mesh) stationary and methanol/chloroform 5:95 v/v as the mobile phases to obtain the compound **MS 4** as a thick red gum that solidified after standing at room temperature for a few days. Yield: 0.87 g (93%). Mp: was not measured.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.695 (d, $J = 4$ Hz, 2H), 8.56 (s, 2H), 7.59–7.53 (m, 8H), 7.50 (d, $J = 16$ Hz, 2H), 7.47 (d, $J = 16$ Hz, 2H), 7.41 (d, $J = 8$ Hz, 2H), 7.16–7.11 (m, 2H), 7.00 (d, $J = 16$ Hz, 2H), 6.55 (s, 2H), 6.55 (s, 6H), 3.88 (s, 6H), 3.86 (s, 3H), 3.17 (t, 8H), 1.54–1.46 (p, 8H), 1.36–1.26 (m, 8H), 0.91 (t, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$, C-type based on DEPT-135 spectrum): $\delta$ 156.3 (C), 151.8 (C), 149.5 (CH), 147.5 (C), 146.0 (C), 138.9 (C), 134.8 (C), 133.2 (CH), 127.4 (CH), 126.7 (CH), 126.0 (C), 125.8 (CH), 125.3 (CH), 123.9 (CH), 121.1 (CH), 119.0 (C),
118.3 (CH), 110.3 (CH), 105.4 (CH), 56.5 (OMe), 56.3 (OMe), 52.4 (CH₂), 29.3 (CH₂), 20.5 (CH₂), 14.1 (CH₃).

HRMS (MALDI–TOF/TOF, positive mode): \( m/z \) calcd. 938.571 (M⁺). Found: 939.673 (M+H)⁺.


4,4’–bis(4–(2,5–dimethoxy–4–(pyrrolidin–1–yl)styryl)styryl)–2,2’–bipyridine (MS 5).

The synthesis of this compound follows the same procedure as described for MS 1. Aldehyde 12b (0.74 g, 2.2 mmol) was used instead of aldehyde 7a. The compound MS 5 was isolated as orange microcrystalline solid. Yield: 0.72 g (87%). Mp (DTA): 274 °C.

\(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 8.68 (d, \( J = 8 \) Hz, 2H), 8.56 (s, 2H), 7.54 (s, 8H), 7.50 (d, \( J = 16 \) Hz, 2H), 7.47 (d, \( J = 16 \) Hz, 2H), 7.41 (d, \( J = 8 \) Hz, 2H), 7.16–7.11 (unresolved, 4H), 6.94 (d, \( J = 16 \) Hz, 2H), 6.31 (s, 2H), 3.88 (s, 6H), 3.86 (s, 6H), 3.41 (unresolved, 8H), 1.96 (unresolved, 8H).

\(^13\)C NMR was not possible because of low solubility.

HRMS (MALDI–TOF/TOF, positive mode): \( m/z \) calcd. 822.415 (M⁺). Found: 823.575 (M+H)⁺.

Anal. calcd. for C₅₄H₅₄N₄O₄: C, 78.80; H, 6.61; N, 6.81. Found: C, 78.96; H, 6.54; N, 6.68.

4,4’–bis(2,5–dibutoxy–4–(4–dibutylaminostyryl)styryl)–2,2’–bipyridine (MS 6). The synthesis of this compound follows the same procedure as described for MS 2. Aldehyde 13b (1.0 g, 2.2 mmol) was used instead of aldehyde 5b. The crude product was purified by a short silica gel column (100–200 mesh) eluting with methanol/chloroform 5:95 v/v as the mobile phase. The compound MS 6 was isolated as a thick red gel that solidified to an orange
solid after standing overnight at room temperature. Yield: 1.1 g (95%). Mp: was not measured.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.675 (d, $J = 4$ Hz, 2H), 8.52 (s, 2H), 7.80 (d, $J = 16$ Hz, 2H), 7.455 (d, $J = 4$ Hz, 2H), 7.42 (d, $J = 8$ Hz, 4H), 7.28 (d, $J = 16$ Hz, 2H), 7.20 (d, $J = 16$ Hz, 2H), 7.15 (s, 2H), 7.14 (s, 2H), 7.10 (d, $J = 16$ Hz, 2H), 6.66 (d, $J = 8$ Hz, 4H), 4.11 (t, 4H), 4.07 (t, 4H), 3.31 (t, 8H), 1.93–1.87 (p, 8H), 1.66–1.57 (m, 16H), 1.41–1.36 (m, 8H), 1.08 (t, 12H), 0.99 (t, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$, C-type based on DEPT-135 spectrum): $\delta$ 156.6 (C), 151.8 (C), 150.6 (C), 149.4 (CH), 147.9 (C), 146.6 (C), 129.8 (CH), 129.4 (C), 128.4 (CH), 128.0 (CH), 125.6 (CH), 125.1 (C), 124.3 (C), 120.3 (CH), 118.9 (CH), 118.2 (CH), 111.7 (CH), 111.1 (CH), 109.8(CH), 69.2 (CH$_2$), 50.8 (CH$_2$), 31.7 (CH$_2$), 29.6 (CH$_2$), 20.4 (CH$_2$), 19.6 (CH$_2$), 14.1 (CH$_3$).

HRMS (MALDI–TOF/TOF, positive mode): $m/z$ calcd. 1106.759 (M$^+$). Found: 1107.748 (M+H$^+$).
Anal. calcd. for C$_{74}$H$_{98}$N$_4$O$_4$: C, 80.25; H, 8.92; N, 5.06. Found: C, 80.15; H, 8.78; N, 4.91.

4,4′–bis(2,5–dibutoxy–4–(2,5–dimethoxy–4–dibutylaminostyrlyl)styryl)–2,2′–bipyridine (MS 7). This compound was synthesized following the same procedure as described for MS 2. The aldehyde 14b (1.2 g, 2.2 mmol) was used instead of aldehyde 5b. The crude product was purified by a short silica gel column (100–200 mesh) eluting with methanol/chloroform 5:95 v/v as the mobile phase. The compound MS 7 was isolated as a red gum that solidified to a red solid after standing for five days at room temperature. Yield: 1.1 g (90%). Mp: was not measured.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.675 (d, $J = 4$ Hz, 2H), 8.51 (s, 2H), 7.51–7.46 (m, 4H), 7.37 (d, $J = 16$ Hz, 2H), 7.21 (d, $J = 16$ Hz, 2H), 7.18 (s, 2H), 7.14 (s, 4H), 6.53 (s, 2H), 4.12 (t, 4H), 4.08 (t, 4H), 3.88 (s, 6H), 3.87 (s, 6H), 3.17 (t, 8H), 1.92–1.86 (m, 8H), 1.66–1.59 (m, 8H), 1.54–1.47 (m, 8H), 1.34–1.27 (m, 8H), 1.08–1.01 (m, 12H), 0.92 (t, 12H).
\[ ^{13}\text{C} \text{NMR (100 MHz, CDCl}_3, \text{ C-type based on DEPT-135 spectrum):} \delta 156.5 (\text{C}), 151.8 (\text{C}), 151.7 (\text{C}), 150.8 (\text{C}), 149.3 (\text{CH}), 147.6 (\text{C}), 146.6 (\text{C}), 140.9 (\text{C}), 129.3 (\text{C}), 128.4 (\text{CH}), 125.8 (\text{CH}), 124.8 (\text{C}), 124.0 (\text{CH}), 121.1 (\text{CH}), 120.4 (\text{CH}), 119.7 (\text{C}), 118.9 (\text{CH}), 111.2 (\text{CH}), 110.5 (\text{CH}), 110.3 (\text{CH}), 105.4 (\text{CH}), 69.1 (\text{CH}_2), 56.4 (\text{OMe}), 56.2 (\text{OMe}), 52.4 (\text{CH}_2), 31.7 (\text{CH}_2), 31.6 (\text{CH}_2), 29.4 (\text{CH}_2), 20.6 (\text{CH}_2), 19.6 (\text{CH}_2), 14.1 (\text{CH}_3). \]

HRMS (MALDI–TOF/TOF, positive mode): \( m/z \) calcd. 1226.801 (M⁺). Found: 1227.884 (M+H⁺).

Anal. calcd. for C\(_{78}\)H\(_{106}\)N\(_4\)O\(_8\): C, 76.31; H, 8.70; N, 4.56. Found: C, 76.25; H, 8.78; N, 4.46.

4,4′-bis(2,5-dibutoxy-4-(2,5-dimethoxy-4-(pyrrolidin-1-yl)styryl)styryl)-2,2′-bipyridine (MS 8). This compound was synthesized following the same procedure as described for MS 2. The aldehyde 15b (1.1 g, 2.2 mmol) was used instead of aldehyde 5b. The crude product was purified by a short silica gel column (100–200 mesh) eluting with methanol/chloroform 5:95 v/v as the mobile phase. The compound MS 8 was isolated as a red–brown solid. Yield: 1.0 g (89%).

Mp (DTA): 202 ºC.

\[ ^1\text{H} \text{NMR (400 MHz, CDCl}_3): \delta 8.675 (d, J = 4 Hz, 2H), 8.51 (s, 2H), 7.80 (d, J = 16 Hz, 2H), 7.49 (d, J = 16 Hz, 2H), 7.45 (unresolved, 2H), 7.32 (d, J = 16 Hz, 2H), 7.22–7.14 (m, 8H), 6.32 (s, 2H), 4.12 (t, 4H), 4.07 (t, 4H), 3.88 (s, 6H), 3.85 (s, 6H), 3.42 (unresolved, 8H), 1.96 (unresolved, 8H), 1.92–1.87 (m, 8H), 1.66–1.60 (m, 8H), 1.06 (t, 12H). \]

\[ ^{13}\text{C} \text{NMR (100 MHz, CDCl}_3, \text{ C-type based on DEPT-135 spectrum):} \delta 156.6 (\text{C}), 152.5 (\text{C}), 151.8 (\text{C}), 150.7 (\text{C}), 149.4 (\text{CH}), 146.6 (\text{C}), 144.2 (\text{C}), 140.8 (\text{C}), 129.7 (\text{C}), 128.4 (\text{CH}), 125.7 (\text{CH}), 124.5 (\text{C}), 124.1 (\text{CH}), 120.3 (\text{CH}), 119.6 (\text{CH}), 118.9 (\text{CH}), 116.5 (\text{C}), 111.3 (\text{CH}), 110.8 (\text{CH}), 110.2 (\text{CH}), 99.8 (\text{CH}), 69.3 (\text{CH}_2), 69.2 (\text{CH}_2), 56.8 (\text{OMe}), 56.5 (\text{OMe}), 50.5 (\text{CH}_2), 31.7 (\text{CH}_2), 31.6 (\text{CH}_2), 25.1 (\text{CH}_2), 19.5 (\text{CH}_2), 14.0 (\text{CH}_3). \]

HRMS (MALDI–TOF/TOF, positive mode): \( m/z \) calcd. 1110.645 (M⁺). Found: 1111.670 (M+H⁺).
Anal. calcd. for C_{70}H_{86}N_{4}O_{8}: C, 75.64; H, 7.80; N, 5.04. Found: C, 75.49; H, 7.68; N, 5.12.

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Spectrum 4.2. $^1$H NMR spectrum of MS 2
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Spectrum 4.4. $^1$H NMR spectrum of MS 3
Spectrum 4.5. $^{13}$C NMR spectrum of MS 3
Spectrum 4.6. $^1$H NMR spectrum of MS 4
Spectrum 4.7. $^{13}$C NMR spectrum of MS 4
Spectrum 4.8. $^1$H NMR spectrum of MS 5
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Spectrum 4.14. $\text{^{13}C}$ NMR spectrum of MS 8