APPENDIX

➢ $^1$H NMR

➢ $^{13}$C NMR

➢ FABMS/MALDITOF MS

➢ FT-IR
IPYF1 (3’ Indolyl – 1’ (4-nitrophenyl) pyrazolino [60] fullerene)

$^1$HNMR spectra of IPYF1

$^{13}$CNMR of IPYF1
FAB-MS of IPYF1

FTIR of IPYF1
IPYF2 (3’ Indoly – 1’ (2, 4-dinitrophenyl) pyrazolino [60] fullerene)

$^1$HNMR spectra of IPYF2

$^{13}$CNMR spectra of IPYF2
**FAB-MS of IPYF2**

**FTIR of IPYF2**
FEFPY (Ferrocene derivatized Fulleropyrrolidine)

HNMR spectra of FEFPY

$^{13}$C NMR of FEFPY

214
FTIR of FEFPY

Peak of Schiff base linkage

FAB-MS of FEFPY
$^1$H NMR spectra of DBCFPY

$^{13}$C NMR of DBCFPY
FAB-MS of DBCFPY

FTIR of DBCFPY
STFPY1 (diamino s-triazine derivatized fulleropyrrolidine)

$^1$HNMR spectra of STFPY1

$^{13}$CNMR of STFPY1
**FAB-MS of STFPY1**

**FTIR of STFPY1**
STFPY2 (amino, methylamino s-triazine derivatized fulleropyrrolidine)

$^1$HNMR spectra of STFPY2

$^{13}$CNMR of STFPY2
FAB-MS of STFPY2

FTIR of STFPY2
STFPY3 (bis(methylamino) s-triazine derivatized fulleropyrrolidine)

$^1$HNMR spectra of STFPY3

$^{13}$CNMR of STFPY3
**FAB-MS of STFPY3**

**FTIR of STFPY3**
STFPY4 (methylamino, dimethylamino s-triazine derivatized fulleropyrrolidine)

\[ ^1H \text{NMR spectra of STFPY4} \]

\[ ^{13} \text{C NMR of STFPY4} \]
FAB-MS of STFPY4

FTIR of STFPY4
STFPY5 (bis(dimethylamino) s-triazine derivatized fulleropyrrolidine)

$^1$HNMR spectra of STFPY5

$^{13}$CNMR of STFPY5
**FAB-MS of STFPY5**

**FTIR of STFPY5**
STFPY6 (bis(ammonium) s-triazine derivatized fulleropyrrolidine)

$^1$HNMR spectra of STFPY6

$^1$CNR of STFPY6
**FAB-MS of STFPY6**

**FTIR of STFPY6**
INHFPY (Isoniazid derivatized fulleropyrrolidine)

$^1$HNMR spectra of INHFPY

$^{13}$CNMR of INHFPY
MALDITOF-MS of INHFPY

FTIR of INHFPY
LFPY (Lysine derivatized fulleropyrrolidine)

\[ \text{HNMR spectra of LFPY} \]

\[ \text{\textsuperscript{13}CNMR of LFPY} \]
**FTIR of LFPY**

**FAB-MS of LFPY**
PYMF (Pyridine functionalized methanofullerene)

$^1$HNMR spectra of PYMF

$^{13}$CNMR of PYMF
FAB-MS of PYMF

FTIR of PYMF
Fullerene–ferrocene dyad linked by rigid bilinkage: synthesis, photophysical properties and application as copper ion sensor

Anish Kumar* and Shobhana K. Menon**

A novel fullerene–ferrocene based donor-bridge-acceptor dyad was synthesized and characterized by elemental analysis, FT-IR, 1H NMR, 13C NMR and FAB-MS. The dyad with a bilinker comprising of azomethine and ester group was studied for its photo physical properties using absorption spectra and steady-state fluorescence spectra as a function of dielectric constant of the medium. Fluorescence spectra of the dyad studied with excitation at 449 nm showed a weak emission at 742 nm, which got weaker on increasing the dielectric constant of the medium, indicating efficient electron transfer from ferrocene to fullerene. By designing a bilinked structure between the two redox moieties, we obtained a chelating structure which was found to coordinate copper ion efficiently and hence found application as a metal ion sensor. Copyright © 2008 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: artificial photosynthesis; dyads; fulleropyrrolidine; metal complexation; sensor.

INTRODUCTION

Artificial photosynthesis based on purple bacteria involves light harvesting by antenna centers and subsequent electron transfer in reaction centers and hence could be used for efficient conversion of solar energy into light energy. The factors that favor electron transfer to readily are small reorganization energy (Δtr ~ 0.2 eV) of photosynthetic reaction center and well balanced electronic coupling between each donor and acceptor. Because of the importance and complexity of natural photosynthesis, it becomes necessary to study simpler models, which can mimic photosynthesis and can efficiently process solar energy. Artificial photosynthesis can be achieved by supramolecular dyads containing electron donors and acceptors linked by covalent linkage. Fullerene-based dyads have been successfully designed and synthesized for such applications. Buckminsterfullerenes possess remarkably physical and chemical properties that make them interesting building blocks for supramolecular assemblies.23,24 C60, a truncated icosahedron, because of its triply degenerate, low lying LUMO at ~4.3 eV is an excellent electron acceptor capable of accepting as many as six electrons reversibly. The delocalization of charges (electrons or holes) within the giant spherical carbon framework (diameter ~7 Å) as well as rigid structure of the spherene offers unique opportunities for stabilizing charged entities. Even in highly reduced state like tetra anion and pent anion, reductive force experienced by the incoming electron is less. The spherical fullerenes accelerates photo induced electron transfer and charge shift, but slows down charge recombination.

The small reorganization energies along with small spherical and rigid structure make it possible to produce a long lived charge separated state with a high quantum yield in donor-fullerene system.9-12 Photocative donor-bridge-fullerene dyads are generally based on chromophore donor moieties such as aniline,11,41 carotenoids,17 TTTF, tetrathiafulvalene,18 porphyrins,19-22 zincporphyrins,125 phthalocyanines,24,26 ferrocenes,25 imidadaoporphyrins,25,26 chlorins,25,26 coumarins,27-29 oligofluorenes,32 oligothiophenes,35 oligoazulenes,35 pyrophosphobides,36 ruthenocenes,38 tetrapyrromes,144 bis(bipyrryl) benzene,29 and tetracene.34 Fullerenes based compounds have also shown potential application in photovoltaic devices and light emitting diode.37 Different monolinkers, both flexible as well as rigid, were tried to enhance the rate of charge separation in fullerene-ferrocene dyads.38

Although some of these dyads containing mesogenic groups in them have shown application as liquid crystal.24,36 Such dyads have not been studied for other applications. There are few reports where fullerene based dyads have been used as metal ion sensor.41-43 The prospect of making better dyad with potential applications as compared to earlier reported ones prompted us to design and synthesize a fullerene ferrocene based dyad (Figs 1 and 2) in which the two redox moieties are joined by bilinkage. By introducing a bilinker with different functionalities such as Schiff base linkage and ester group we obtained a chelating structure that can readily form complexes with metal ions.

We report herein the synthesis, photo physical and electrochemical properties of the dyad and its application as a metal ion sensor.
The synthetic methodology, derivatives of 1-naphthyl were synthesized from 2AG through two 1J.5 truncation and a series of new derivatives were synthesized using the Schif base methodology. The compounds were screened for their antibacterial activity against several strains of bacteria. The activity of the compounds was found to be dependent on the nature of the substituent on the naphthyl group. The compounds were found to be active against Gram-negative bacteria, particularly those resistant to commonly used antibiotics. The most active compound was found to be effective against a wide range of bacteria, including those resistant to traditional antibiotics. This suggests that these derivatives could be useful as potential antibiotic agents in the treatment of infections caused by multidrug-resistant bacteria.
Fullerene Isoniazid Conjugate – A Tuberculostat with Increased Lipophilicity: Synthesis and Evaluation of Antimycobacterial Activity

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A fullerene-isoniazid conjugate has been synthesized by 1,3 dipolar cycloaddition reaction of fullerene (C60) with isonicotinic acid (4-formylbenzoyl) hydrazide and N-methylglycine. The identity and purity of the compound was confirmed by elemental analysis, 1H NMR, 13C NMR and MALDI-TOF mass spectral analysis. Stable water suspension, in which the particles of the synthesized conjugate were made to aggregate in nanosize, was successfully tested for antimycobacterial activity against Mycobacterium avium and strains of Mycobacterium tuberculosis - H37Rv & H6/99 at concentration as low as 0.50 μg/mL.

Key words: antimycobacterial, drug design, fullerene, isonicotinic acid, nanosize.

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According to World Health Organization, tuberculosis is one of the leading cause of death infecting nine million people globally with three million deaths every year (1). Emergence of resistant and sensitive strains have made clear the pressing need for the evolution of newer and more powerful drugs, re-examination and the re-evaluation of older ones along with detailed elucidation of the different modes of antimicrobial activity (2). A detailed study of structure-active relationship had revealed that hydrophilic feature was crucial for determining antimicrobial activity and a more hydrophilic character of the compound could definitely increase the antibacterial potency (3). In general the log P values for the most active compounds are in the range of 5.86–7.06. Hypothetical that a further increase of lipophilicity (higher log P values) could improve activity as facilitating entrance through the lipid rich mycobacterial membrane could be checked by introduction of highly lipophilic moiety (like fullerene C60). With a very appealing chemical as well as physical property fullerene has been exploited in many fields ranging from biological fields to material sciences (4). Interaction of carbonfullerene with proteins as well as the interaction of fullerene-based nanomaterials with lipid barrier protein has been some of the major breakthroughs of the molecule in the field of medicinal chemistry (5). Biologically active fullerene derivatives are still a field of immense research with the latest developments being the attachment of heterocyclic entities to C60 resulting in excellent antibacterial activity (6). Although there are several reports of biologically active fullerene derivatives, there is only one report where conjugation of fullerene with a well-known drug has resulted in enhancement of biological activity (7). Apart from the core fullerene derivatives reported by Bao et al, no reports have come up of fullerene derivatives as antibacterials. Hence, these are some of the areas which can be further explored in the already well established fullerene chemistry in parallel, isoniazid (INH) is a well-known drug with pronounced activity against Mycobacterium tuberculosis. Mycobacterium bovis and Mycobacterium africanum and Mycobacterium microti at minimum inhibitory concentration (MIC) ranging from 0.25 to 0.50 μg/mL (8). Several studies on the mechanism of action suggest that INH inhibits the biosynthesis of cell wall mycolic acids, thereby making the mycobacteria susceptible to reactive oxygen radicals and other environmental factors (9). The first line antibacterial drug INH is a prodrug requiring activation in the mycobacterial cell by the catalase/peroxidase activity of katG gene product. N-Acetyl
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