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Abstract

A series of new functionalized fulleropyrrolidines with varied alkyl chains were synthesized and characterized using various spectral techniques. The properties of supramolecular architecture core C_{60} was fine-tuned by the incorporation of mono- and di- alkyl chains attached via phenyl ring attached with pyrrolidine ring. Long alkyl chains attached [60] fullerene exhibited more solubility, high emission and absorption.

1. Introduction

Over the past two decades, fullerene chemistry has been directed to create cage like carbon structures as building block in organic synthesis for several important applications.[1–3] Among the various fullerenes reported C_{60} is widely studied and it shows a high range of interesting features, which include the spherical shape of fullerene bringing about to delocalized π-electron systems. C_{60} is also a good electron acceptor in both ground and excited states, used in the construction of photovoltaic devices[4] because of their unique electrochemical properties, namely ability to accept up to six electrons.[5] Apart from that, it is an excellent photosensitizer due to its long-lived triplet state, high absorption in the visible region, appearance of various stable oxidation states and the low degree of charge recombination. Chemical modification of fullerenes has been ardently explored because of their potential applications in biological activities such as, anti-HIV activity, neuroprotective, DNA

cleavage, anti-oxidant and anti-microbial activities.[6] Moreover it is used as organic semiconductors, photoconductors, photovoltaic devices, electronic and optical devices.[7,8]

Modification of fullerene structures using synthetic methods is a new custom structure approach to control the morphology of fullerenes. Fulleropyrrolidine consists of a variety of organo-fullerene derivative in which, a pyrrolidine ring is fused to a 6,6-junction of the fullerene structure which is a widely studied fullerene derivative.[9] These derivatives have been prepared by 1,3-dipolar cycloaddition of azomethine ylides to C_{60} known as Prato reaction.[10] A number of C_{60} fulleropyrrolidines have been synthesized by reaction of C_{60} with N-substituted glycine and suitable aldehydes.[11]

One of the major problem with fullerene derivatives, especially C_{60} is its poor solubility in organic solvents and insoluble nature in water. This attitude hinders their application in the solar cells[12] and solution based organic electronic devices.[13]To overcome this obstacle, two different routes have been handled to increase the solubility.[14] The first strategy is that the fullerene molecules are converted into soluble host molecules[15] by non-covalently encapsulation method. Another method is the covalent functionalization of fullerene by the substitution of various groups through chemical modification.[16,17]Accordingly chemical modification in fullerene derivatives has not only alter the physical and chemical properties but also provides useful insight for molecular constructions. In this article an efficient synthesis, characterization and photo-physical aspects of functionalized new fulleropyrrolidines are reported.

2.Results and discussion

Prato reaction is an example of [3 + 2] cycloaddition reaction, in which the azomethine ylide is generated *in situ* after decarboxylation of iminium salts obtained by condensation of amino acid and aldehydes. These ylides react with the C_{60} to form fulleropyrrolidines. The synthesis of fulleropyrrolidine **4** is described in Scheme **2** to **4**. It is obtained by condensation of

appropriate benzaldehyde **3** (Scheme 1) and N-methylglycine onto C_{60}. Table 1 describes the product yield **4a-4i** and C_{60} recovered after the column chromatography. Various alkyl chains were introduced onto the pyrrolidine ring through the lateral phenylic group. The introduction of alkyl chains will enhance the van der Waals interaction among the molecules and improve molecular connectivity. The power conversion efficiency of organic solar cells based on fullerene derivatives was reported to increase with the length of substituted aliphatic chains.[17,18]These fullerene derivatives are divided into two parts, sp^2 carbon rich C_{60} moiety and sp^3 aliphatic chain. C_{60} contains carbon atoms with three sp^2 hybrid orbitals having one delocalized π-orbital such as benzene. As a result, it has a high affinity towards aromatic solvents such as toluene, xylene, and benzene but low affinity to aliphatic and polar solvents. However, aliphatic chains are usually soluble in sp^3-carbon rich solvents like hexane, alcohols and ethers. Although both the parts are hydrophobic in nature, but shows different affinities to several solvents.

The structure of the synthesized compounds was confirmed by FT-IR, ^{1}H and ^{13}C NMR spectral data. The FT-IR spectra of the **4a–i** shows the occurrence of chemical reaction, which are characterized by the disappearance of characteristic aldehydic peaks at 1677, 1387, 1298 cm^{-1} and appearance of C–N stretching peak at 1026 cm^{-1}. The aliphatic C–H stretching peaks appeared at 2921, 2849 cm^{-1}, C=C stretching peak observed at 1607 cm^{-1}, C–O–C stretching peak reported at 1265 cm^{-1}, aromatic C–H, wagging peaks appeared at 827, 718 cm^{-1}. In addition the characteristic peaks of C_{60} observed at 1375, 1176 cm^{-1} as well as a C_{60} cage vibration peak was noted at 525 cm^{-1}. ^{1}H NMR spectra of **4a–i** shows (Table 2) the presence of pyrrolidine protons as singlet at 2.73–2.81 ppm and the two doublets in the region of 4.14–5.48 ppm (d, J ~ 8.4–10.8 Hz). The ArCHN proton signal appeared at 4.84–5.48 ppm, aromatic ring proton signals are observed at 6.89–7.82 ppm (J = 6.89–8.40 Hz), alkyl chain proton peaks are observed in the region of 0.90–1.97 ppm as

multiplets. Methyl protons peak appeared as a triplet at 0.80 ppm. The ^{13}C NMR spectra of **4a–i** show the signals in the region between 129.0–156.0 ppm thus indicating C_{2v} symmetry of the fullerene moiety. A peak was seen near 83ppm,corresponding to the sp^3 hybridized carbon atom with a 6,6 ring junction on the fullerene core. N–CH_3 group signal appeared around at 40.0 ppm and signals for alkyloxy chains were observed between 14.0–70.0 ppm. Furthermore the other peaks between14-27 ppm belongs to the alkyl groups present in the fullerene derivatives.

2.1 Electrochemical studies

The electrochemical characterization of the compound **4c** was performed at room temperature in 0.5M tetrabutylammonium perchlorate (TBAP) in $CHCl_3$ solution, using three electrode cell unit, a glassy carbon as working electrode, a platinum wire as counter electrode and Ag/AgCl as reference electrode. The experiment was done under the scan rate of 0.5 mV/s and the current sensitivity $100mVs^{-1}$. This method is very useful to get information about the electronic structure of fulleropyrrolidines. The electron acceptor properties of [60] fullerene,[19] which include the ability to reversibly undergo up to six one-electron reduction. [20] The **Fig. 1** shows the redox potential of compound **4c** with three reversible reduction points which is potentially shifted to more negative values due to the saturation of one of the double bond on the fullerene C_{60} cage. This should raise the LUMO energy of the ensuring fullerene derivative.[21] Thus, the reduction peaks of **4c** were observed at -0.923,-1.132, -1.951 V, more negative values than the [60] fullerene -0.60, -1.00, -1.52, -2.04 V reported by Nazario Martin et al.[22] Reduction potential of fulleropyrrolidine is slightly higher than C_{60}, suggests that the parent C_{60} has more tendency to accept electrons.

2.2 Photophysical studies

In UV absorption spectra the sharp absorption bands appeared at 285 nm and 325 nm are (**Fig. 2)** characteristic signs of fullerene C_{60} mono adduct.[23]The new shoulder observed at 432 nm corresponds to the fulleropyrrolidine. In addition a weak characteristic absorption band observed at 703 nm, indicates the S_1--->S_0 transition[24] of C_{60} moiety. When compare the **4c** spectrum with the parent $C_{60,}$the peaks observed at 284, 336, 405 nm of C_{60} were totally dissimilar except the peak at 284nm. The peak observed at 284 nm is the characteristic peak of [60] fullerene.

The fluorescence spectra of **4c** and the reference compound C_{60} were measured with 365 nm excitation in toluene.The fulleropyrrolidine exhibits greater fluorescence intensity than parent $C_{60.}$On comparison, **4c** has more than two fold increase in emission than that of C_{60} under the same concentration. This shows the lowering of the symmetry of C_{60} by derivatization which considerably increase the fluorescence intensity of the fullerene compound.[24,25]Further, the characteristic high emission in fluorescence spectra is due to the addition of the alkyl chain in the C_{60} core(**Fig. 3).** A sharp peak appeared at 732 nm is due to interaction between alkyl group singlet excited state and fullerene ground state.[26] Corroborate this peak also assigned as a (6, 6) - region addition on the fullerene. Compound **4c** shows high emission in fluorescence spectra compare with other alkylated fulleropyrrolidines. Because the long alkyl chain substitution rationally may bring out more emission out off others. The chain length had an important impact on the fluorescence spectra of the compounds. Good efficiency and high electron rich properties make these compounds suitable for OLED devices. Due to light emitting and charge transporting capacity of this kind of alkylated π-compounds have encountered increasing attention in recent years for application in flexible organic electronics.[27, 28]

The resulted spectroscopic techniques, anticipate that the appropriate hybridization design of alkyl chains attached with fullerene moiety can direct the self-organized supramolecular structure as a fundamental subunit. In addition, generally the fullerene derivatives are known to show poor electron acceptor properties than the parent C_{60}, which occurs as a result of the saturation of double bond in the C_{60} framework which in turn raised the LUMO energy level.[21]Israelachvili*et al.* reported the different ratios of both C_{60} and alkyl tail groups which results in a different aggregation naturally as considered by the self-assembly theory for typical amphiphilic surfactants in aqueous media.[29]Therefore, these design and development in alkyl group concepts are anticipated to produce novel alkylated compounds with coveted new applications in optoelectronic devices such as OLED.

3. Experimental

3.1. General

Buckminsterfullerene, C_{60} (+99.95%), 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 1-bromohexadecane, 1-bromodecane, 1-bromooctadecane, K_2CO_3, sarcosine were purchased from Aldrich and used without further purification. N,N′-Dimethylformamide, toluene, chloroform, dichloromethane, hexane were used as reagent grade without further purification. Thin layer chromatography was carried on Merck $60F_{254}$ silica gel plate and column chromatography was performed with Merck silica gel (100–200 mesh).

The ^{1}H and ^{13}C spectra were recorded on BrukerAvance 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard. IR spectra were recorded on Nicolet Avatar 300 FT-IR spectrophotometer. MALDI- TOF MS were processed on an applied Biosystems voyager DE-PRO spectrometer. Which is equipped with a nitrogen laser (λ=337nm) operated in positive ion, linear mode. DCTB (3-methyl-4-(4-tert-butylphenyl)butadiene-1,1-dinitrile) matrix solution (10 mg/ML DCTB in 1mL of toluene) used as a matrix. A cyclic

Voltammetry experiment was performed by using three electrode cell units, consisting of polished 2mm a glassy carbon as working electrode, a platinum wire as counter electrode and Ag/AgCl reference electrode. Tetrabutylammonium perchlorate (TBAP) was added as a supporting electrolyte. Cyclic Voltammetry were performed with CHI604C instrument, under the scan rate of 0.5 mV/s and the current sensitivity given was $100mVs^{-1}$. The experiment was done at room temperature in a dry and inert atmosphere, accomplished by passing nitrogen gas for about 10min before starting the experiment. The UV-visible spectral measurements were carried out with a Shimadzu Model UV-1650 UV-visible spectrophotometer. The fluorescence emission spectra were monitored by using a Shimadzu RF-5310PC spectrofluorimeter with the excitation slit width of 5.0nm. Both UV-visble and fluorescence measurements were carried out in 10mm quartz cells.

3.2. Synthesis of functionalized benzaldehydes

Suitable benzaldehyde **1** (10 mmol) and alkyl halide **2** (20 mmol) were dissolved in 40 mL of N,N′-dimethylformamide and K_2CO_3 (5.52 g, 40 mmol) was added. The solution was stirred at room temperature for 24 h, and then the reaction mixture was poured into a mixture of water and dichloromethane. The organic layer was separated and dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude product was purified on a column chromatography using dichloromethane and hexane (8:2 v/v) as eluent.

3.2.1. 2,4-bis(n-hexadecyloxy)benzaldehyde, ***3a***. FT-IR (KBr, cm^{-1}) ν 2920, 2850, 1677, 1606, 1467, 1387, 1298, 1267, 1192, 1113, 1019, 860, 719; ^{1}H NMR ($CDCl_3$, 400 MHzδ ppm) 0.65 (bs, 6H), 1.03–1.22 (m, 60H), 1.60 (m, 4H), 3.79 (bs, 4H), 6.19 (s, 1H), 6.28 (d, 1H, J = 8.2 Hz), 7.56 (d, 1H, J = 8.4 Hz), 10.10 (s, 1H);^{13}C NMR ($CDCl_3$, 100 MHzδ ppm)14.12, 22.70, 25.97, 26.06, 28.19, 28.78, 29.03, 29.10, 29.37, 29.45, 29.56, 29.60, 29.67, 29.70, 31.93, 32.86, 34.05, 68.42, 68.48, 98.95, 106.18, 118.92, 130.19, 163.38, 165.79, 188.44.

3.2.2. 3,4-Bis(n-decyloxy)benzaldehyde, ***3b***. FT-IR (KBr, cm^{-1}) *ν*2921, 2851, 1685, 1591, 1465, 1439, 1394, 1275, 1236, 1134, 1066, 1019, 807, 724; ^{1}H NMR ($CDCl_3$, 400 MHzδppm) 0.88 (t, 6H), 1.27–1.47 (m, 36H), 1.84 (m, 4H), 4.06 (m, 4H), 6.95 (d, 1H, *J* = 8.0 Hz), 7.41 (d, 2H, *J* = 12.4 Hz), 9.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHzδppm) 14.14, 22.71, 25.97, 26.01, 28.21, 28.80, 29.00, 29.09, 29.31, 29.38, 29.41, 29.47, 29.53, 29.60, 29.62, 29.64, 31.91, 31.94, 32.87, 34.07, 69.13, 110.91, 111.74, 126.64, 129.87, 149.44, 154.69, 191.04.

3.2.3. 3,4-Bis(n-octadecyloxy)benzaldehyde, ***3c***. FT-IR (KBr, cm^{-1}) *ν*2919, 2850, 1685, 1591, 1457, 1439, 1278, 1237, 1134, 1017, 808, 722; ^{1}H NMR ($CDCl_3$, 400 MHzδppm) 0.87 (d, 6H), 1.25–1.47 (m, 56H), 1.84 (d, 4H, *J* = 6.4 Hz), 4.06 (d, 4H, *J* = 7.6 Hz), 6.95 (d, 1H, *J* = 8.0 Hz), 7.40 (d, 2H, *J* = 12.4 Hz), 9.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHzδppm) 14.16, 22.73, 25.98, 26.02, 29.01, 29.09, 29.41, 29.66, 29.71, 29.76, 31.97, 69.14, 110.89, 111.72, 126.66, 129.86, 149.44, 154.69, 191.07.

*3.2.4. 2,3,4-Tris(n-heptyloxy)benzaldehyde,****3d***. FT-IR (KBr, cm^{-1}) *ν*2927, 2858, 1681, 1587, 1456, 1375, 1292, 1182, 1089, 800; ^{1}H NMR ($CDCl_3$, 400 MHzδppm) 0.80 (s, 9H), 1.65–1.27 (m, 20H),1.71 (m, 6H), 3.88 (t, 2H), 3.94 (t, 2H), 4.08 (t, 2H), 6.62 (d, 1H, *J* = 8.8 Hz), 7.47 (d, 1H, *J* = 8.8 Hz), 10.16 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHzδppm) 14.04, 18.35, 22.45, 22.58, 22.63, 25.96, 26.00, 26.07, 27.82, 28.11, 28.42, 28.59, 29.01, 29.10, 29.17, 29.19, 29.35, 29.68, 30.15, 30.29, 30.93, 31.62, 31.76, 31.78, 31.87, 32.82, 33.74, 58.16, 68.85, 73.66, 75.23, 76.83, 108.01, 123.43, 123.67, 141.00, 156.63, 157.01, 159.10, 188.89.

3.2.5. 4-Decyloxybenzaldehyde, ***3e***. FT-IR (KBr, cm^{-1}) *ν*2926, 2855, 1694, 1602, 1465, 1391, 1310, 1257, 1160, 1106, 1020, 832, 723; ^{1}H NMR ($CDCl_3$, 400 MHzδppm) 0.88 (t, 3H), 1.27–1.48 (m, 16H), 1.80 (m, 2H), 4.03 (t, 2H), 6.98 (d, 2H, *J* = 8.8 Hz), 7.81 (d, 2H, *J* = 8.8 Hz), 9.86 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHzδppm) 14.13, 21.02, 22.70, 22.87, 25.83, 25.93, 25.98, 28.20, 28.52, 28.62, 28.80, 29.07, 29.21, 29.28, 29.34, 29.36, 29.57, 31.91, 32.86, 53.47, 64.13, 64.68, 68.44, 114.75, 128.34, 129.74, 131.99, 161.23, 164.29, 171.26, 190.82.

3.2.6. 4-Octadecyloxybenzaldehyde, ***3f***. FT-IR (KBr, cm^{-1}) *ν*2922, 2852, 1686, 1602, 1468, 1309, 1254, 1157, 1015, 833, 722; ^{1}H NMR ($CDCl_3$, 400 MHzδ ppm) 0.87 (t, 3H), 1.25–1.48 (m, 32H), 1.80 (m, 2H), 4.03 (t, 2H), 6.98 (d, 2H, *J* = 8.4 Hz), 7.82 (d, 2H, *J* = 8.4 Hz), 9.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.16, 22.74, 26.00, 29.09, 29.39, 29.41, 29.59, 29.63, 29.71, 29.75, 31.97, 68.44, 114.75, 129.74, 132.01, 164.30, 190.84.

*3.2.7. 3-Methoxy-4-octadecyloxybenzaldehyde,****3g***.FT-IR (KBr, cm^{-1}) *ν*2912, 2848, 1676, 1636, 1589, 1464, 1402, 1264, 1136, 1026, 863, 724, 653; ^{1}H NMR ($CDCl_3$, 400 MHzδ ppm) 0.87 (t, 3H), 1.25–1.46 (m, 30H), 1.88 (m, 2H), 3.93 (s, 3H), 4.09 (t, 2H), 6.96 (d, 1H, *J* = 8.0 Hz), 7.42 (t, 2H), 9.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.14, 22.72, 25.91, 28.93, 29.38, 29.55, 29.60, 29.72, 31.95, 56.06, 69.22, 109.24, 111.36, 126.86, 129.86, 149.86, 154.23, 190.96.

3.3. Synthesis of fulleropyrrolidine4

A mixture of **3a** (1 mmol), C_{60} (0.50 mmol) and 66 mg of sarcosine (0.75 mmol) in 40 mL of toluene was refluxed till its colour turned from purple into reddish brown. The solvent was removed under reduced pressure and the reaction mixture was directly purified on a column chromatography using toluene/hexane 2:1 as an eluent.

3.3.1. *N-methyl-2-(2,4-bis(n-hexadecyloxy)phenyl)fulleropyrrolidine,* ***4a.*** FT-IR (KBr, cm^{-1}) *ν*2921, 2849, 1607, 1460, 1375, 1265, 1176, 1111, 1026, 827, 718, 525;^{1}H NMR ($CDCl_3$, 400 MHzδ ppm) 0.87 (t, 6H), 1.24–1.43 (bs, 56H), 1.75 (m, 4H), 2.79 (s, 3H),3.95 (m, 4H), 4.27 (d, 1H, *J* = 9.2 Hz), 4.95 (d, 1H, *J* = 9.2 Hz), 5.46 (s, 1H), 6.46 (s, 1H), 6.58 (d, 1H,*J* = 8.4 Hz), 7.82 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.16, 22.72, 29.39, 29.73, 31.96, 39.94, 68.44, 68.51, 74.28, 82.78, 130.28, 135.52, 135.52, 137.92, 141.17, 143.12, 144.02, 144.14, 144.18, 144.29, 144.34, 144.71, 144.99, 145.19, 145.30, 145.32, 145.40, 145.73, 145.78, 146.54, 146.78, 148.06, 148.32, 149.37, 149.90, 155.04.

3.3.2. N-Methyl-2-(3,4-bis(n-decyloxy)phenyl)fulleropyrrolidine, ***4b***. FT-IR (KBr, cm^{-1}) ν2922, 2852, 1627, 1462, 1263, 1128, 1021, 871, 520; ^{1}H NMR ($CDCl_3$, 400 MHz δppm) 0.87 (bs, 6H), 1.25–1.42 (m, 34H), 1.77 (m, 4H), 2.81 (s, 3H), 3.98 (bs, 4H), 4.23 (d, 1H, J = 10.8 Hz), 4.85 (s, 1H), 4.97 (d, 1H, J = 9.2 Hz), 6.94 (d, 2H), 7.39 (s, 1H), 7.62 (d, 1H);^{13}C NMR ($CDCl_3$, 100 MHzδppm) 14.15, 22.72, 23.77, 26.08, 29.16, 29.34, 29.40, 29.50, 29.65, 29.73, 31.96, 40.07, 68.99, 69.06, 69.38, 69.99, 70.01, 83.46, 129.26, 135.79, 139.69, 141.59, 141.71, 142.06, 142.27, 142.59, 142.71, 143.17, 144.42, 144.69, 145.26, 145.57, 145.81, 145.97, 146.18, 146.34, 146.54, 146.97, 147.32.

3.3.3. N-Methyl-2-(3,4-bis(n-octadecyloxy)phenyl)fulleropyrrolidine, ***4c***. FT-IR (KBr, cm^{-1}) ν2921, 2852, 1736, 1630, 1463, 1282, 1101, 1022, 876, 723, 613; ^{1}H NMR ($CDCl_3$, 400 MHzδppm)0.87 (t, 6H), 1.25 (bs, 64H), 1.79 (m, 4H), 2.81 (s, 3H), 3.97 (t, 2H), 4.06 (t, 2H),4.24 (d, 1H, J= 9.6 Hz), 4.84 (s, 1H), 4.97 (d, 1H, J = 9.2 Hz), 6.88 (bd, 1H, J = 7.6 Hz), 6.94 (d, 1H, J = 8.0 Hz), 7.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHzδppm) 14.17, 22.73, 26.05, 29.08, 29.14, 29.19, 29.33, 29.41, 29.42, 29.51, 29.68, 29.75, 29.78, 31.97, 40.07, 69.00, 69.06, 69.36, 70.01, 76.73, 83.46, 129.25, 135.78, 136.49, 140.13, 141.71, 141.85, 142.06, 142.09, 142.14, 142.16, 142.19, 142.27, 142.58, 142.60, 142.62, 142.71, 143.00, 143.17, 144.42, 144.68, 144.72, 145.18, 145.27, 145.30, 145.32, 145.37, 145.49, 145.53, 145.57, 145.81, 145.95, 145.98, 146.12, 146.16, 146.18, 146.24, 146.28, 146.34, 146.53, 146.96, 147.32, 153.68, 154.18, 156.31;MALDI-TOF mass calculated 1390.7 found 1389.2.

3.3.4. N-Methyl-2-((2,3,4-tris(n-heptyloxy))phenyl)fulleropyrrolidine, ***4d***. FT-IR (KBr, cm^{-1}) ν2922, 2852, 1593, 1456, 1382, 1292, 1219, 1176, 1089, 1026, 840, 771, 669, 526; ^{1}H NMR ($CDCl_3$, 400 MHzδ ppm)0.84 (t, 9H), 1.22–1.32 (m, 30H), 1.77 (m, 6H), 2.78 (s, 3H), 3.87 (t, 2H), 3.96 (m, 2H), 4.10 (bs, 1H), 4.25 (d, 1H, J = 9.6 Hz), 4.96 (d, 1H, J = 9.6 Hz), 5.38 (s, 1H), 6.74 (d, 1H, J = 8.8 Hz), 7.59 (d, 1H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.15, 14.25, 22.64, 22.68, 22.77, 26.05, 26.13, 26.31, 29.14, 29.23, 29.30, 29.45, 29.73, 30.02, 30.55, 31.83, 31.91, 32.05, 40.16, 68.62, 69.19, 69.97, 73.31, 73.83,

76.38, 76.72, 108.41, 122.44, 124.19, 136.62, 139.46, 140.09, 141.31, 141.65, 141.88, 142.22, 142.31, 142.65, 143.12, 144.47, 144.62, 145.26, 145.33, 145.57, 145.96, 146.09, 146.27, 147.31, 152.65, 153.10, 154.10; MALDI-TOF mass calculated 1196.4 found 1195.4.

3.3.5. N-Methyl-2-((4-decyloxy)phenyl)fulleropyrrolidine, ***4e***. FT-IR (KBr, cm^{-1}) ν2918,2850, 1607, 1460, 1370, 1242, 1169, 1112, 1029, 823, 722, 550. ^{1}H NMR ($CDCl_3$, 400 MHzδ ppm)0.87 (t, 3H), 1.25–1.44 (m, 18H), 1.76 (t, 2H), 2.79 (s, 3H), 3.95 (t, 2H), 4.23 (d, 1H, J = 9.2 Hz), 4.87 (s, 1H), 4.97 (d, 1H, J = 9.2 Hz), 6.94 (d, 2H, J = 8.0 Hz), 7.69 (bs, 2H); ^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.17, 22.74, 26.11, 28.99, 29.20, 29.36, 29.41, 29.47, 29.61, 29.74, 31.93, 31.97, 33.87, 40.03, 68.01, 69.00, 70.01, 83.25, 114.11, 114.53, 128.68, 130.49, 135.80, 136.59, 136.80, 139.33, 139.61, 139.92, 140.14, 140.18, 141.56, 141.71, 141.86, 142.04, 142.14, 142.31, 142.57, 142.70, 143.00, 143.17, 144.42, 144.65, 144.73, 145.17, 145.26, 145.36, 145.58, 145.82, 145.97, 146.18, 146.34, 146.43, 146.56, 146.86, 147.33, 153.71, 154.17, 156.42, 159.22.

3.3.6. N-Methyl-2-((4-octadecyloxy)phenyl)fulleropyrrolidine, ***4f***. FT-IR (KBr, cm^{-1}) ν2918, 2850, 1607, 1460, 1370, 1242, 1169, 1112, 1029, 832, 723, 544, 526. ^{1}H NMR ($CDCl_3$, 400 MHzδ ppm)0.87 (d, 3H), 1.25 (m, 32H), 2.02 (t, 2H), 2.79 (s, 3H), 3.94 (t, 2H), 4.23 (d, 1H, J = 9.2 Hz), 4.87 (s, 1H), 4.95 (d, 1H, J = 9.2 Hz), 6.94 (d, 2H,J = 7.6 Hz), 7.70 (bs, 2H);^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.15, 22.72, 26.10, 29.19, 29.39, 29.73, 31.95, 33.85, 40.04, 68.95, 68.98, 69.01, 83.25, 128.69, 128.88, 130.00, 134.46, 136.82, 136.97, 138.97, 139.32, 140.17, 140.18, 142.05, 142.12, 142.14, 143.00, 143.16, 143.44, 144.42, 145.26, 145.57, 146.16, 146.34, 146.55, 147.60, 147.62, 147.76, 148.28, 148.89, 150.13, 152.42, 153.02.

3.3.7.N-Methyl-2-((3-methoxy-4-octadecyloxy)phenyl)fulleropyrrolidine, ***4g***. FT-IR (KBr,cm^{-1}) ν 2922, 2852, 1629, 1589, 1458, 1382, 1265, 1128, 1028, 767, 669, 526; ^{1}H NMR ($CDCl_3$, 400

MHzδ ppm) 0.86 (d, 3H), 1.25–1.42 (m, 32H), 1.85 (m, 2H), 2.82 (s, 3H), 3.88 (s, 3H), 3.99 (t, 2H), 4.25 (d, 1H, J = 9.2 Hz), 4.86 (s, 1H), 4.98 (d, 1H, J = 9.6 Hz), 6.89 (d, 1H, J = 7.6 Hz), 7.35 (s, 1H), 7.53 (d, 1H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.14, 22.71, 26.71, 26.00, 29.23, 29.38, 29.46, 29.58, 29.63, 29.72, 30.07, 30.22, 31.46, 31.95, 40.07, 56.27, 68.97, 70.03, 83.49, 135.77, 136.47, 139.83, 140.20, 141.85, 142.06, 142.27, 142.61, 143.01, 143.20, 144.42, 144.72, 145.30, 145.57, 145.81, 145.96, 146.17, 146.29, 146.51, 147.33, 153.65, 154.17;MALDI-TOF mass calculated 1152.3 found 1151.

3.3.8. N-Methyl-2-((2,4,6-trimethyl)phenyl)fulleropyrrolidine, ***4h***. FT-IR (KBr, cm^{-1}) ν2921, 2852, 1742, 1611, 1457, 1374, 1172, 1123, 1023, 852, 729, 526; ^{1}H NMR ($CDCl_3$, 400 MHzδ ppm)2.25 (s, 3H), 2.59 (s, 3H), 2.73 (s, 3H), 3.06 (s, 3H), 4.14 (d, 1H, J = 9.6 Hz), 5.00 (d, 1H, J = 8.4 Hz), 5.48 (s, 1H), 6.89 (d, 2H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHzδ ppm) 14.15, 20.87, 22.72, 22.79, 22.87, 28.99, 29.39, 29.73, 31.96, 33.85, 40.11, 69.69, 69.98, 70.22, 80.67, 130.14, 132.52, 138.36, 141.17, 141.53, 142.09, 142.18, 142.60, 143.13, 145.29, 145.32, 145.62, 145.82, 145.97, 146.06, 146.18, 146.27, 146.96, 147.29, 151.54, 153.57, 154.70, 157.29; MALDI-TOF mass calculated 895.9 found 895.9.

3.3.9. N-Methyl-2-((4-tert-butyl)phenyl)fulleropyrrolidine, ***4i***.FT-IR (KBr, cm^{-1}) ν2918, 2848, 1737, 1674, 1591, 1462, 1373, 1288, 1176, 1093, 1024, 837, 721, 526; ^{1}H NMR ($CDCl_3$, 400 MHzδppm)1.25–1.30 (m, 9H), 2.80 (s, 3H), 4.25 (d, 1H, J = 9.2 Hz), 4.91 (s, 1H), 4.98 (d, 1H, J = 9.6 Hz), 7.42 (d, 2H, J = 7.6 Hz), 7.70 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHzδppm) 14.16, 22.73, 29.19, 29.40, 29.73, 31.37, 31.96, 34.66, 40.15, 69.11, 70.10, 83.42, 125.52, 128.76, 129.00, 133.76, 135.77, 136.76, 140.18, 141.53, 141.70, 141.86, 142.01, 142.07, 142.12, 142.29, 142.58, 142.69, 144.42, 144.62, 144.73, 145.26, 145.47, 145.56, 145.96, 146.14, 146.24, 146.33, 146.43, 146.54, 146.95, 147.32, 151.41, 153.69, 154.23.

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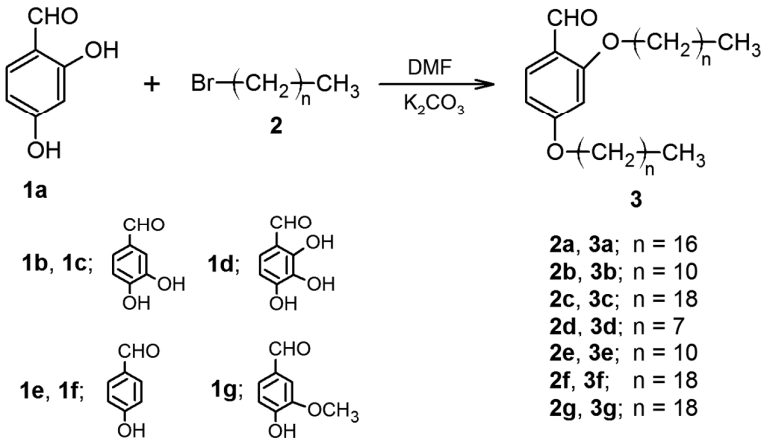
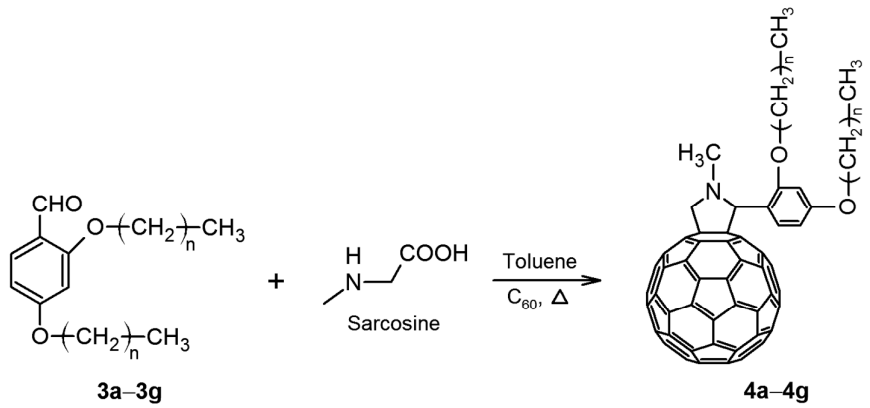
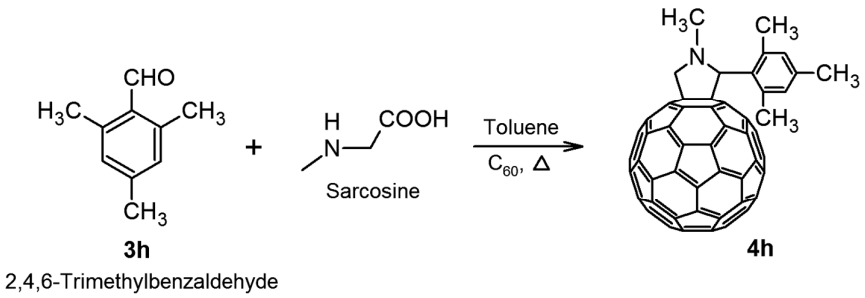
Electronic supplementary information (ESI) available



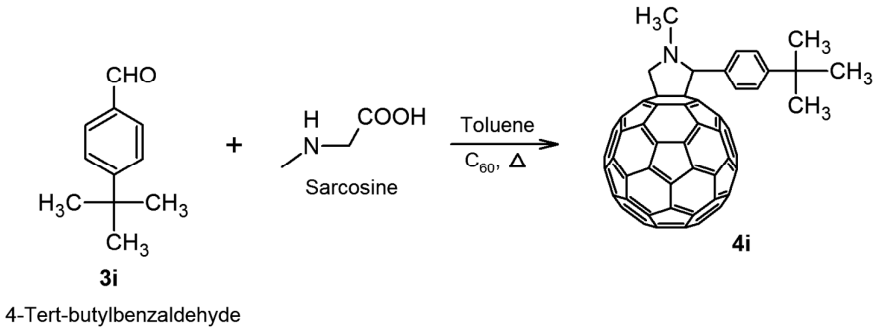
Scheme 1 Synthesis of aldehyde derivatives **3a-3g**.



Scheme 2 Synthetic schedule of fulleropyrrolidines **4a-4g**.



Scheme 3 Synthesis of **4h**.



Scheme 4 Synthesis of **4i**

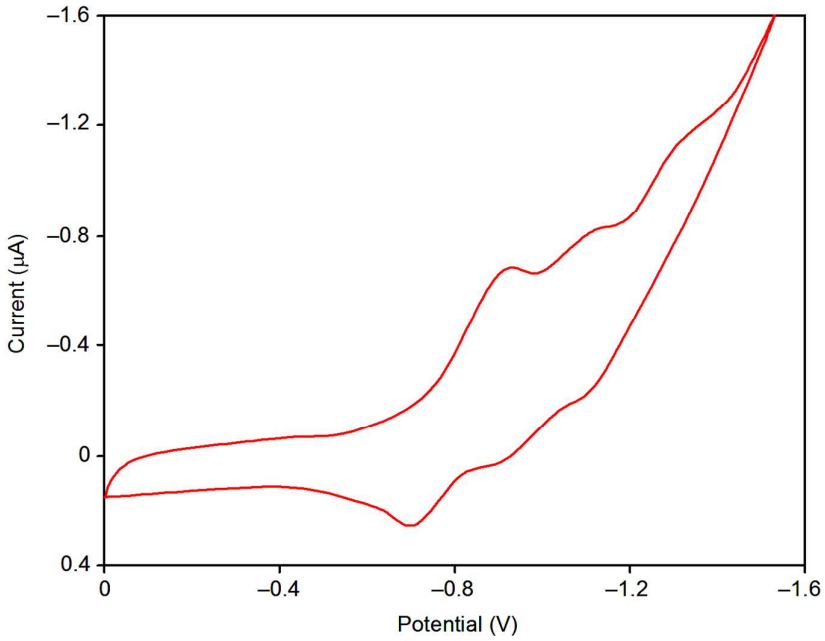


Fig. 1 Cyclic voltammogram of **4c** in $CHCl_3$, 0.5 M TBAP, scan rate100mV/s.

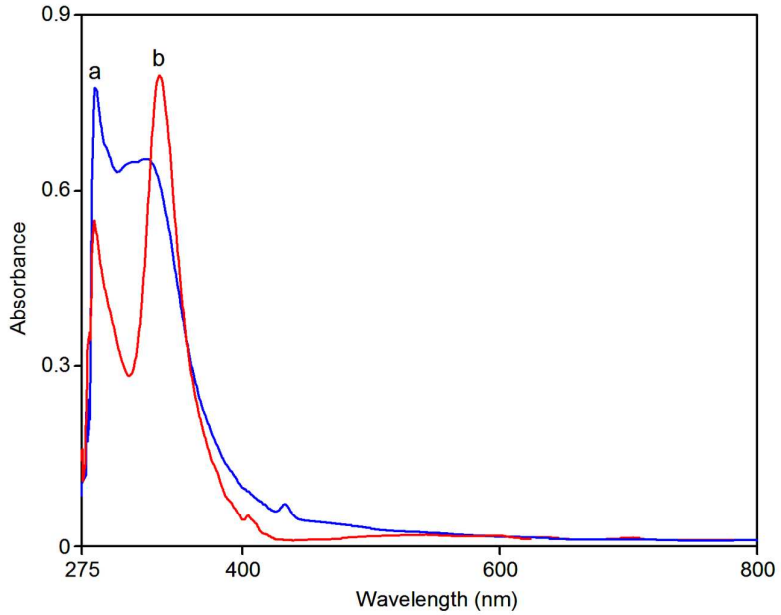


Fig. 2 UV-vis absorption spectra of **4c** (a) and C_{60} (b) in toluene at $1x10^{-6}$mol/L.

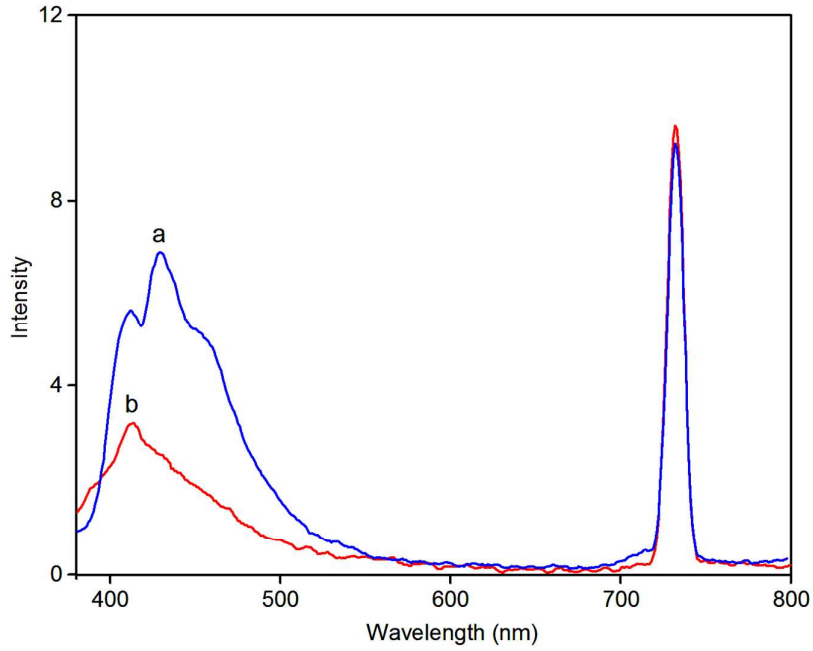


Fig. 3 Fluorescence spectra of 4c (a) and C_{60} (b) in$1x10^{-6}$mol/L in toluene.

Table 1 Product yield, reaction time and recovered C_{60} for the cycloaddition reactions of C_{60} with N-methylglycine and aldehydes.

Aldehyde	Reaction time (h)	Product	Yield (%)	Recovered C_{60} (%)
3a	9	**4a**	34	40
3b	13	**4b**	31	38
3c	15	**4c**	29	42
3d	15	**4d**	32	37
3e	18	**4e**	31	41
3f	17	**4f**	32	39
3g	13	**4g**	31	35
3h	16	**4h**	30	40
3i	17	**4i**	28	39

Table 2 ^{1}H NMR spectral data for fulleropyrrolidine derivatives **4a–4i.**

Compound	N-Me	H–2	H–5a (J/Hz)	H–5b (J/Hz)
4a	2.79	5.46	4.27 (9.2)	4.95 (9.2)
4b	2.81	4.85	4.23 (10.8)	4.97 (9.2)
4c	2.81	4.84	4.24 (9.6)	4.97 (9.2)
4d	2.78	5.38	4.25 (9.6)	4.96 (9.6)
4e	2.79	4.87	4.23 (9.2)	4.97 (9.2)
4f	2.79	4.87	4.23 (9.2)	4.95 (9.2)
4g	2.82	4.86	4.25 (9.2)	4.98 (9.6)
4h	2.73	5.48	4.14 (9.6)	5.00 (8.4)
4i	2.80	4.91	4.25 (9.2)	4.98 (9.6)

Notes and references

1. In: *The Fullerenes*. Kroto, H. W.; Fisher, J. E.; Cox, D. E.; Eds., Perga
2. Nakanishi, T.; Schmitt, W.; Michinobu, T.; Kurth, D. G.; Ariga, K. *Chem. Commun.* **2005**, *48*, 5982–5984.
3. Miller, M. L.; West, R. *Chem. Commun.* **1999**, *18*, 1797–1798.
4. Li, W.; Zhu, X.; Wang, J.; Liang, R.;. Li, J.; Liu, S.; Tu, G.; Zhu, J. *J. Colloid&Inerface Sci*. **2014**, *418*, 81-86.
5. Arias, F.; Xie, Q.; Wu, Y.; Lu, Q.; Wilson, S.R.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 6388–6394.
6. Bakry, R.; Vallant, R. M.; Najam-Ul-Haq, M.; Rainer, M.; Szabo, Z.; Huck, C. W.; Bonn, G. *Int. J. Nanomed.* **2007**, *2*, 639–649.
7. Tanigaki, K.; Ebbesen, T. W.; Saito, S.; Mizuki, J.; Tsai, J. S.; Kubo, Y.; Kuroshima, S. *Nature.* **1991**,*352*, 222–223.
8. Zielinska, A.; Leonowicz, M.; Li, H.; Nakanishi, T. *J. Current Opinion inColloid& Interface Sci.* **2014**, *9*, 131-139.
9. Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519–526.
10. Muller, D.; Zeltser, I.; Bitan, G.; Gilon, C. *J. Org. Chem.* **1997**, *62*, 411–416.
11. Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P. M.; Koch, A.; Echert, H.;Srdanov, G.; Webb, H. M. *Am. Chem. Soc. Symp. Series* **1992**, *481*, 161–175.
12. Page, Z. A.; Liu, Y.; Duzhko, V. V.; Russell, T. P.; Emrick. T. *Science.***2014**, *346*, 441-444.
13. Da Ros, T.; Prato, M. *Chem. Commun.* **1999**, *8*, 663–669; (b) Tagmatarchis, N.; Prato, M.*Synlett*.**2003**,*6*, 768–779.
14. Kumar, A.; Rao, M. V.; Menon, S.K. *Tetrahedron Lett.***2009**, *50*, 6526–6530.
15. Yamakoshi, Y. N.; Yagami, T.; Fukuhara, K.; Sueyoshi, S.; Miyata, N. *J. Chem. Soc. Chem. Commun.* **1994**, 517–518.
16. Chiang, L. Y.; Bhonsle, J. B.; Wang, L.; Shu, S. F.; Chang, T. M.; Hwu, J. R. *Tetrahedron*.**1996**, *52*, 4963–4972.
17. Lee, J.-K.; Fujida, K.; Tsutsui, T.; Kim, M.-R. *Sol. Energy Mater. Sol. Cells*.**2007**, *91*, 892–896.

18. Zhang, X.; Li, X. L.; Ma, L. X.; Zhang, B. *Rsc Adv*. **2014**, *4*, 60342-60348.

19. Kratschmer, W.; Lamb, L. D.; Fostiropoulos, F.; Huffman, D. R. *Nature.***1990**, *347*, 354–358.

20. Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978–3980.

21. Suzuki, T.; Maruyama, T.; Akasaba, T.; Ando, W.; Kobyashi, K.; Nagase, S. *J. Am. Chem. Soc.***1994**, *116*, 1359-1363.

22. Illescas, B.M.; Martin, N. *J. Org. Chem.***2000**, *65*, 5986-5995.

23. Zhang, P.; Guo, Z. X.; Lv, S. *Chinese Chem. Let*. **2008**, *19*, 1039-1042.

24. Lin, S. K.;Shiu, L. L.; Chien, K.M.; Luh, T. Y.; Lin, T. I. *J. Phy. Chem*. **1995**, *99*, 105-111.

25. Williams, R. M.; Zwier, J. M.; Verhoeven, J. W. *J. Am. Chem. Soc*. **1995**, *117*, 4093-4099.

26. Mukherjee, S.; Bauri, A. K.; Bhattacharya, S. *Spectrochim. Acta A*. **2013**, *109*, 32-36.

27. Hollamby, M. J.; Nakanishi, T. *J Mater Chem.***2013**, *1*, 6178–83.

28. Zielinska, A.; Leonowicz, M.; Li, H.; Nakanishi, T. *Current Opinion in Colloid & Interface Science.* **2014***, 19*, 131-139.

29. Murakami, H.; Nakanishi, T.; Morita, M.; Taniguchi, N.; Nakashima, N.; *Chem. Asian J.* **2006**, *1*, 860–867.

Efficient synthesis of highly soluble and functionalized fulleropyrrolidines

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New functionalized fulleropyrrolidines with high emission and absorption.