SYNTHESIS AND SPECTRAL INVESTIGATIONS OF COVALENTLY LINKED PHTHALOCYANINE-C_{60} DYAD VIA FLEXIBLE CARBON LINKER

Daisuke Sukeguchi, Hideyuki Yoshiyama, Surya Prakash Singh, Norio Shibata,* Shuichi Nakamura, Takeshi Toru,* Yasuhiko Hayashi, and Tetsuo Soga

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya, 466 8555, Japan. Fax: +81-52-735-5442; Tel: +81-52-735-7543;
E-mail: nozshiba@nitech.ac.jp, toru@nitech.ac.jp

Abstract: Phthalocyanine-C_{60} dyad **1** via a flexible saturated carbon linker was synthesized. The UV/Vis and fluorescence spectra studies of **1** revealed that intramolecular, not intermolecular, photoinduced electronic communication was observed in the solution state. We also examined UV-Vis and fluorescence spectra of a mixture of C_{60} and conventional tetra *tert*-Bu phthalocyanine **2** for comparison

Keywords: phthalocyanine, fullerene, hybrid molecule, flexible carbon linker, electronic communication

Introduction

There is a great interest in developing novel materials for photovoltaic applications such as solar cells [1]. Upon light absorption, these materials should generate charge-separate states with high efficiency. In this context, molecular systems incorporating electron donors and electron acceptors have been actively investigated [2]. Selection and combination of donor and acceptor-type organic materials play a key role in the photovoltaic devices, and fullerenes such as C_{60} have gained a prestigious position as acceptors in this area [2-5]. On the other hand, organic dyes have been proposed to be promising partners for donor-type materials [6]. Among the various organic dyes have been prepared for this purpose, phthalocyanines have become one of the most adaptable building blocks due to their intense absorptions and in the UV/violet and in the red /near-IR spectral regions as well as electrochemical and photochemical stabilities [7]. The incorporation of phthalocyanines into photovoltaic devices is usually performed in blends together with acceptor fullerenes [8-12]. In 1995, Linssen et al reported the first covalently bonded fullerene-phthalocyanine complex as "green fullerene", in which the unique electronic properties of C_{60} were disclosed [13]. Since then, an interest in covalently bound fullerene-functionalized phthalocyanines has been increasing. Nowadays, several unsymmetrical metal phthalocyanine-C_{60} conjugates via a flexible [14, 15] or rigid [16-20] linker have been synthesized to study intramolecular processes such as electron and energy transfers between phthalocyanines donor and C_{60} accepter. In connection with our research program aimed at the design and synthesis of functional phthalocyanines [21-25], we required a novel unsymmetrical metal phthalocyanines-C_{60} dyad **1** for the development of thin film solar cells, in which the fullerene is covalently bonded to a terminal position of phthalocyanine via a saturated alkyl chain. The UV/Vis and fluorescence spectra studies of **1** revealed that intramolecular, not intermolecular, photoinduced electroniccommunication was observed in the solution state. We also examined UV/Vis and fluorescence spectra of a mixture of C_{60} and conventional tetra *tert*-Bu phthalocyanine **2** for comparison (Figure 1).

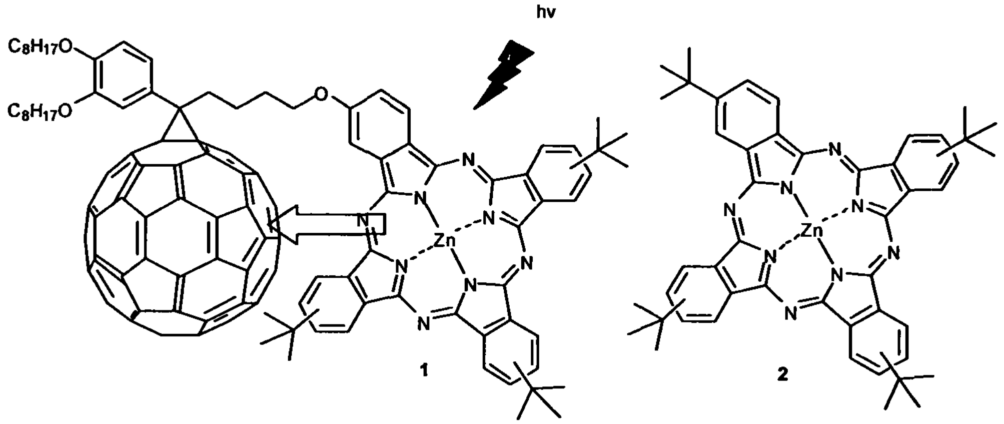
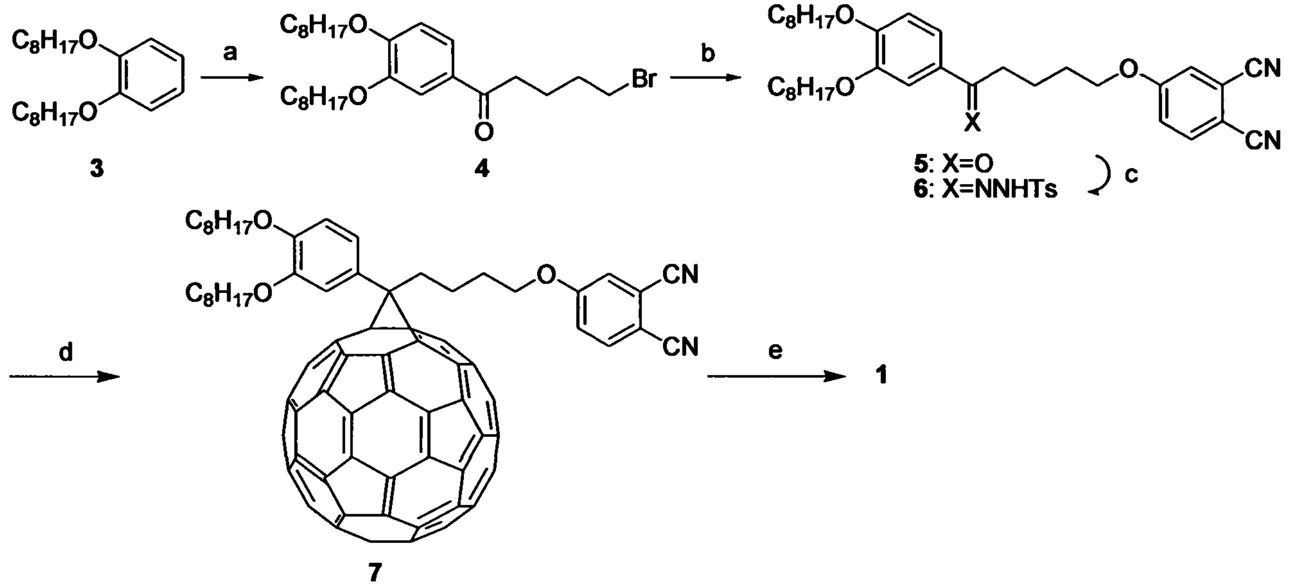


Figure 1: Phthalocyanine-C_{60} dyad **1** and phthalocyanine **2**.

The phenyl ring in **1** was designed to be bis-alkylated with long octyl chains due to overcome the intrinsic solubility problem of the C_{60} and phthalocyanine. The flexible saturated carbon linker could easily induce conformational changes of **1** in the multi-component system, which should be effective for the intramolecular electronic communication between the C_{60} and the phthalocyanine in **1** through space, not through the linker.

Results and Discussion



Scheme 1: Synthesis of **1**: (a) $Br(CH_2)_4COCl$, $AlCl_3$, CH_2Cl_2. 0 °C, 86%. (b) 4-hydroxyphthalonitorile, K_2CO_3, *iso*-butylmethylketone, reflux, 73%. (c) *p*-tosyl hydrazide, MeOH, reflux, 82% (d) NaOMe, pyridine then C_{60}, *o*-DCB, 80 °C, 32%. (e) 4-*tert*-butylphthalonitorile, $ZnCl_2$, 2-dimethylaminoethanol, 130 °C, 4%.

The synthetic route for the compound **1** is shown in Scheme 1. Friedel-Craft acylation of **3** [26] with 5-bromopentanoyl chloride afforded **4** in 86%. Synthesis of 4-[5-(3,4-dioctyloxyphenyl)-5-oxopentyloxy]phthalonitrile dinitrile **5**, was achieved in 73% by the reaction of **4** with 4-hydroxyphthalonitrile in the presence of potassium carbonate in *iso*-butylmethylketone under reflux temperature. Subsequently, the treatment of **5** with *p*-tosylhydrazide yielded the hydrazone **6** after purification by column chromatography on silica-gel (82%). Phthalonitrile **7** was prepared in 32% from **6** in the presence of fullerene in *o*-DCB using sodium methoxide in pyridine. The target phthalocyanine-C_{60} system **1** was finally synthesized; exploring a conventional method. Namely, **7** and excess equivalents of 4-*tert*-butylphthalonitrile were allowed to react with zinc chloride in 2-dimethylaminoethanol at 130 °C for 48 h (Scheme 1). The crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2 to CH_2Cl_2: pyridine=98:2 to furnish **1** as a dark green solid, its identification and purity were confirmed by ^{1}H NMR and analytical reverse-phase HPLC. MALDI-TOF MS spectrum of **1** shows the iso-topic distribution caused by Zn(II) which provides a proof for its characterization (Figures 2 and 3).

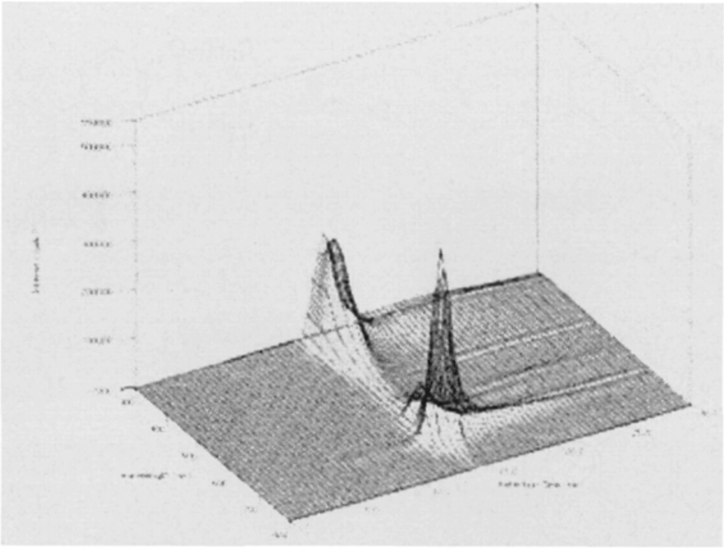


Figure 2: HPLC spectrum of **1**: (H_2O:MeCN:THF=8:42:50, 0.2 mL/min), tR=14.1 min.

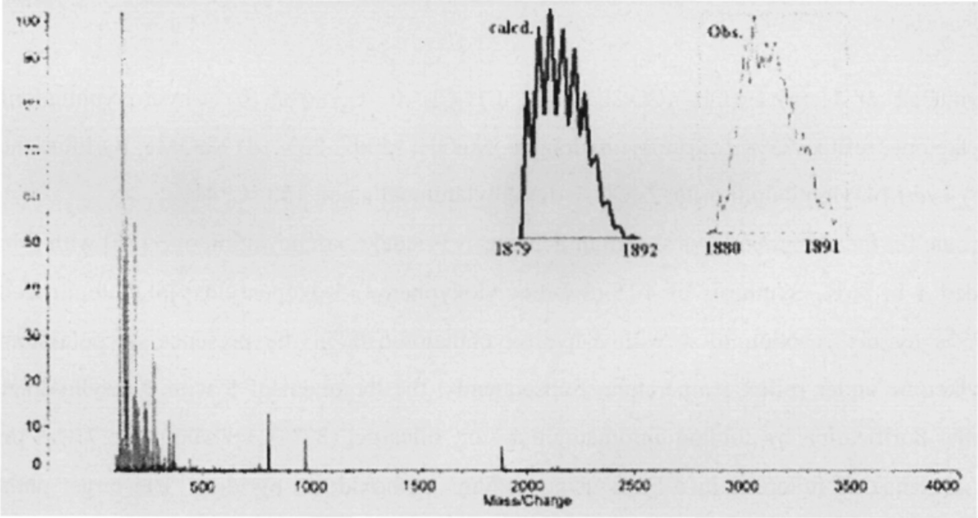


Figure 3: MALDI-TOF MS Chart of **1** (DHB): m/z = 1880-1891 ([M+H+], isotopic pattern).

The phthalocyanine-C_{60} dyad **1** is soluble in *o*-DCB, THF, DMF, 1,4-dioxane and pyridine. With our expectation, the UV-Vis spectrum of **1** in THF shows a Q-band at 671 nm and a Soret band at 333 nm, which indicates the dyad **1** existing as an aggregation-free monomer in solution. The Q-band did not split in spite of the unsymmetrical nature of substituted phthalocyanines [27]. The UV-Vis spectrum of **1** is a superposition of those of **2** and **7**. These results confirmed that the fullerene moiety has less effect on the electronic structure of the phthalocyanine in the ground state (Figure 4).

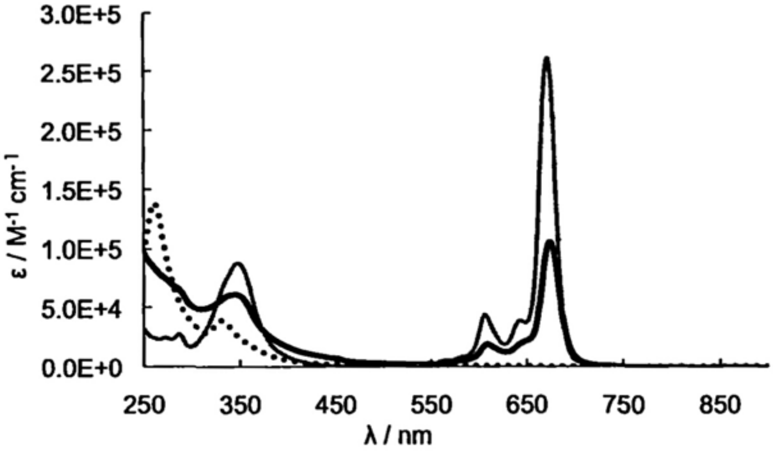


Figure 4: UV-Vis Spectra of **1** (solid line), **2** (gray line) and **7** (dashed line) in THF.

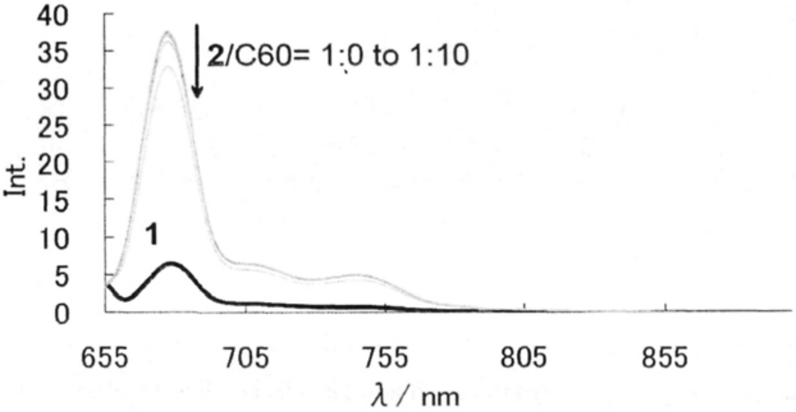


Figure 5: Fluorescence spectra of **1**, **2** and mixture of **2**/C_{60} (**2**:C_{60}=1:0—1:10) in THF.

We next investigated the fluorescence spectra (Figure 5). While general phthalocyanine **2** showed a strong fluorescence at 677 nm (fluorescence quantum yield $\Phi_f = 0.58$), the fluorescence emission of **1** was markedly quenched regardless of the non-aggregation ($\lambda_{em} = 687$ nm; $\Phi_f = 0.07$). In contrast to the photochemistry observed for dyad **1**, the fluorescence was not efficiently quenched for a mixture of **2** and C_{60}, independent of molar ratios (**2**:C_{60}=1:0—1:10). These results clearly indicate the involvement of intramolecular, not intermolecular, electronic communication from phthalocyanine to C_{60} moiety in the quenching process.

Electrochemical studies were finally performed by the differential pulse voltammetry (DPV) using a platinum electrode in THF (Figure 6, Table 1). The results were compared with those of **2** and **7** as reference compounds. Although the DPV of **1** is rather broad and oxidation potentials are not really clear, the reduction potentials of dyad **1** compared with a superposition of those of **2** and **7** are basically similar. This suggests that no electronic coupling prevails between the two electroactive groups of dyad **1** in their singlet ground state. Eventually, an intramolecular electronic communication mechanism of **1** could be explained by the electronic communication from the phthalocyanine excited state to the C_{60} moiety.

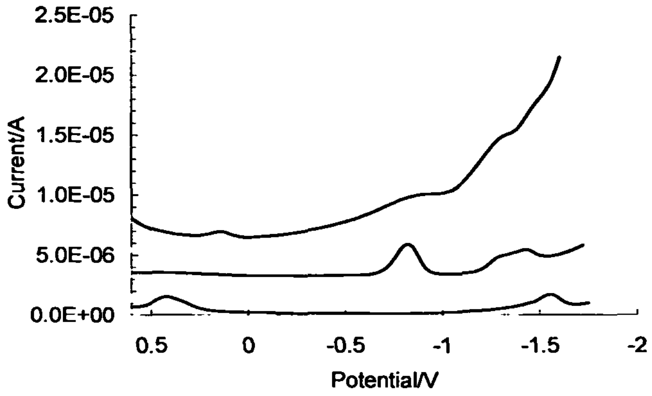


Figure 6: Differential Pulse voltammogram of **1** (top), **7** (middle), **2** (bottom).

Table 1: Peak potentials of **1**, **7**, and **2**.

	E_{OX}	E_{red}^{1}	E_{red}^{2}	E_{red}^{3}
1	0.180	-0.790	-1.240	-1.430
7		-0.800	-1.265	-1.410
2	0.475	-1.505		

Conclusions

In conclusion, the design and synthesis of phthalocyanine-C_{60} dyad **1** have been described. The dyad **1**, regardless of its saturated alkyl linker, appears to be useful material for developing electronic communication between C_{60} and phthalocyanine [28]. The efficiency of **1** for organic thin-film solar cells is under investigations.

Experimental

General

All solvents were dried and distilled according to standard procedures. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica-gel plate (60F-254). Column chromatography was carried out on a column packed with silica gel 60N spherical neutral size 63-210 μm. ^{1}H NMR (200 MHz) spectra were taken on a Varian Gemini-200 spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane. Infrared (IR), UV-vis and steady-state fluorescence spectra were recorded on a JASCO FT/IR-200 Spectrometer, V-530 spectrometer and FP-6200 Fluorospectrometer, respectively. Quantum yields were calculated following the procedure mentioned before [25]. Mass spectra of MALDI-TOF were taken on a SHIMADZU Axima CFR plus. Reverse phase HPLC analyses were performed on a JASCO PU-2080 Plus using 4.6 x 250 mm Develosil ODS-HG-5 column and MD-2015 multiwavelength detector. Electrochemical experiments were carried out on a BAS 50W electrochemical analyzer (Bioanalytical Systems, Inc., West Lafayette, IN 47906, USA). Tetrabutylammonium hexafluorophosphate (TBAPF) was purchased from TCI and recrystallized from EtOH. The solvent THF (Kanto Chemical Co. Inc., tetrahydrofuran, dehydrated stabilizer free) was passed through Glass Contour Ultimate Solvent

System. For CV and DPV, 3 mm platinum was used as working electrode and platinium wire as counter electrode. $Ag/AgNO_3$ (0.01 M in MeCN/0.1 M TBAPF) was used as reference electrode separated by a vycor glass, and all potentials given relate to this electrode. The measurements were performed using a concentration of approximately 0.5 mM of the compounds.

Synthesis of 1-(3,4-Bis-octyloxyphenyl)-5-bromopentan-1-one (4)

5-Bromopentanoyl chloride (1.8 mL, 13.45 mmol) was dissolved in CH_2Cl_2 (7.5 mL). Aluminium trichloride (1.99 g, 14.95 mmol) was added in portions at 0 °C. Subsequently, 1,2-bis-octyloxy benzene (5 g, 14.95 mmol) in CH_2Cl_2 (7.5 mL) was added. The reaction was allowed to stir until the end of visible gas evolution (ca. 45 min). Subsequently, the reaction mixture was stirred for another 20 min at 40 ^{0}C. The reaction mixture turned reddish brown. Cooling to room temperature was followed by removal of the solvent. The product was purified by column chromatography (silica gel; ethyl acetate: hexane= 10:90) to yield **4** (5.35 g, 86%) as white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.55-7.50 (m, 2H), 6.87 (d, J = 7.8, 1H), 4.08 – 4.04 (m, 4H), 3.47 (t, J = 12, 2H), 2.98 (t, J = 13.6, 2H), 2.02 – 1.75 (m, 8H), 1.56– 1.28(m, 20H), 0.88 (t, J = 7.0, 6H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 197.74, 153.17, 148.56, 129.57, 122.34, 112.21, 111.41, 69.22, 37.00, 33.48, 32.40, 31.92, 29.48, 29.14, 29.37, 26.14, 23.28, 22.81, 14.27; Anal. Calcd. $C_{27}H_{45}BrO_3$- C; 65.19, H; 9.05 Found C; 65.09, H; 9.02; FT-IR (KBr): 3073, 3055, 3036, 2923, 2853, 2604, 2312, 2062, 1928, 1845, 1670, 1584, 1514, 1499, 1472, 1429, 1394, 1334, 1294, 1269, 1230, 1173, 1145, 1094, 1081, 1060, 1035, 1014, 991, 918, 878, 816, 800, 627; MS (EI) *m/z* 498.

4-{5-(3,4-dioctyloxyphenyl)-5-oxopentyloxy}benzene-1,2-dinitrile (5)

The compound **4** (3.0 g, 6.04 mmol) and 4-hydroxyphthalonitrile (792 mg, 5.49 mmol) were dissolved in methyl-*iso*-butylketone (10 mL), and potassium carbonate (2.3 g, 16.48 mmol) was added. The solution was heated under reflux for 9 h. Subsequently, the solvent was evaporated in *vacuo*. The solid obtained was partitioned between dichloromethane (DCM) and water. The aqueous phase was extracted with DCM. The combined organic layers were washed with water and evaporated in *vacuo*. Purification by column chromatography (Silica gel; ethyl acetate:hexane= 4:6) yielded **5** (2.56 g, 83%) as white solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.69 (d, J = 8.6, 1H), 7.54 (d, J = 9.8, 2H), 7.24– 7.11 (m, 2H), 6.87(d, J = 8.2, 1H), 4.08 (m, 6H), 3.0 (br, 2H), 1.91 – 1.75 (m, 8H), 1.59–1.28 (m, 20H), 0.90 (t, J = 10.8, 6H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 197.63, 161.67, 153.27, 148.56, 134.86, 129.52, 122.34, 119.33, 119.04, 117.11, 115.48, 115.05, 112.25, 111.43, 106.84, 69.26, 37.31, 31.88, 29.43, 29.41, 29.34, 29.28, 29.15, 28.47 26.10, 22.76, 20.89, 14.22; FT-IR (KBr): 3082, 2952, 2231, 1670, 1592, 1520, 1465, 1380, 1346, 1270, 1188, 1129, 1098, 1018, 969, 879, 837, 818; Anal. Calcd. $C_{35}H_{48}N_2O_4$- C;74.96, H;8.63, N;5.00 Found: C;74.86, H;8.76, N;4.93.; MS (EI) *m/z* 560.

4-{5-(3,4-dioctyloxyphenyl)-5-(2-tosylhydrazono)pentyloxy}benzene-1,2-dinitrile (6)

The compound **5** (857 mg, 1.53 mmol) and *p*-tosyl hydrazide (868 mg, 4.66 mmol) were dissolved in methanol (15 mL). The resulting mixture was heated under reflux and reaction was monitored by TLC (silica gel, ethyl acetate). After 4h, the conversion almost complete. After cooling to room temperature, the solvent was evaporated in *vacuo*. Purification of the residue by column chromatography on silica gel (ethyl acetate:hexane=5:5) yielded **6** (903 mg, 81%) as pale yellow solid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.47 (s, 1H), 7.91 (d, *J* = 8.2, 2H), 7.63 (d, *J* = 8.6, 1H), 7.31-7.03 (m, 6H), 6.79 (d, *J* = 8.4, 1H), 4.03-3.93 (m, 6H), 2.69 (br, 2H), 2.41 (s, 3H), 1.89-1.65 (m, 8H), 1.49-1.21 (m, 20H), 0.91 (t, *J* = 12.6, 6H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 161.66, 156.80, 148.56, 143.94, 135.20, 134.91, 129.67, 129.31, 124.15, 122.38, 119.45, 117.12, 117.03, 115.51, 115.08, 113.67, 112.26, 106.89, 69.55, 68.70, 37.53, 31.93, 31.90, 29.54, 29.36, 29.28, 26.54, 22.79, 21.76, 14.26; FT-IR (KBr):3214, 2921, 2853, 2232, 1600, 1564, 1520, 1488, 1472, 1374, 1327; Anal. Calcd. $C_{42}H_{56}N_4O_5S$- C;69.20, H;7.74, N;7.69, Found: C; 69.11, H,7.97, N;7.63; MS (EI) *m/z* 728.

1'-(3,4-dioctyloxyphenyl)-1'-{4-(3,4-dicyanophenoxy)butyl}-1,2-methano[60]fullerene (7)

The compound **6** (702 mg, 0.963 mmol) was dissolved in pyridine (2.0 mL) and sodium methoxide (52.0 mg, 0.963 mmol) was added. The mixture was stirred for 30 min. at room temperature after which a solution of C_{60} (625 mg, 0.867 mmol) in *ortho*-dichlorobenzene (*o*-DCB) (10 mL) was added. The resulting mixture was stirred at 80 °C for 24 h. After cooling it to room temperature, the solvent was removed in *vacuo* to furnish the residue which was purified by column chromatography (silica gel; ethyl acetate: hexane= 3:7) to yield the precursor of **7**. It was refluxed in toluene for 24 h for isomerization to afford 351 mg of **7** as black solid in 32% yield. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.70 (d, *J* = 8.8, 1H), 7.4 (d, *J* = 7.4, 1H), 7.24 (s, 1H), 7.17 (d, *J* = 11.4, 2H), 6.97 (d, *J* = 8.0, 1H), 4.08 (m, 6H), 2.9 (br, 2H), 1.92 (m, 8H), 1.29 (m, 20H), 0.89 (t, *J* = 5.0, 6H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 161.65, 148.98, 148.78, 148.50, 147.99, 147.62, 146.88, 145.51, 144.86, 144.48, 144.19, 143.98, 143.69, 143.49, 143.31, 142.77, 142.44, 142.10, 141.85, 141.55, 141.34, 141.00, 140.71, 140.14, 139.92, 139.21, 138.77, 138.54, 137.61, 134.93, 128.52, 125.07, 123.77, 119.37, 119.09, 117.25, 117.06, 115.47, 115.03, 112.85, 107.02, 80.26, 69.77, 69.12, 68.80, 68.55, 60.79, 51.91, 35.50, 31.98, 29.46, 28.67, 26.32, 23.67, 22.86, 20.86, 14.34; Anal. Calcd. $C_{95}H_{48}N_2O_3$- C;90.17, H;3.82, N;2.21 Found: C;90.03, H;3.92; N;2.28; MALDI-TOF MS: *m/z* 1264.

C60-tBuPc Dyad (1)

A mixture of **7** (50 mg, 0.0391 mmol), 4-*tert*-butylphthalonitrile (138 mg, 7.51 mmol), $ZnCl_2$ (9.9 mg, 0.158 mmol) and 2-dimethylaminoethanol (0.5 ml) was refluxed for 48 h. After cooling to room temperature, water was added, then filtered it followed by washing with water. A crude product was purified by column chromatography (silica gel; CH_2Cl_2 then CH_2Cl_2: pyridine= 98:2), to yield **1** (3.1 mg, 4%) as greenish solids. ^{1}H NMR (THF-d_8, 200 MHz): δ 6.82-9.46 (brm, 15H), 3.75-4.25 (brm, 6H), 1.69 (bs, 27H), 1.18 (bs, 30H), 0.65-0.85 (brm, 6H); FT-IR (KBr): 670, 750, 831, 921, 1047, 1089, 1257, 1329, 1387, 1489, 1508, 1612, 1718, 2854, 2923, 2954, 3403; UV/Vis (1.0 x 10^{-5} M in THF): λ_{max} (log ε) = 345 (4.78), 608 (4.28), 674 (5.02) nm ; Fluorescence (THF): λ_{em} = 678, 714, 749 nm, Φ_f = 0.07; MALDI-TOF MS (DHB): *m/z* = 1880-1891.

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