Supplementary Material (ESI) for Chemical Communications

Supporting Information

Multistep Electron Transfer Systems Based on Silicon Phthalocyanine, [60]Fullerene and Trinitrofluorenone

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Instrumentation and Materials

All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. Commercial TLC plates (silica gel 60 F254, SDS) were used to monitor the progress of the reaction, with spots observed under UV light at 254 and 365 nm. Column chromatography was performed with silica gel 60A (particle size 40-63 μm, SDS). NMR spectra were taken using a 300 MHz Bruker AC-300. Ultraviolet–visible (UV-vis) absorption measurements were taken on a ThermoSpectronic Helios γ spectrophotometer. Infrared measurements were taken with a Fourier Transform (FT-IR) ThermoNicolet model IR 200 Spectrometer in transmission method with KBr. Mass spectra were obtained from a Bruker Reflex III matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometer using dithranol or DCTB as a matrix.

General Procedure and Compound data

Synthesis of TNF-C_{60}-SiPc-C_{60}-TNF pentad 1:
A mixture of silicon phthalocyanine **2** (9 mg, 0.009 mmol), TNF-C_{60} acid derivative **3** (26 mg, 0.019 mmol), DCC (16 mg, 0.078 mmol) and DMAP (2 mg, 0.016 mmol) in dry dichloromethane (1 mL) was stirred at room temperature under argon atmosphere during 3 days. The solvent was removed under reduced pressure and the product was purified by flash chromatography (SiO_2, $CH_2Cl_2 \rightarrow CH_2Cl_2/Et_2O$ 30:1) to yield compound **1** (6 mg, 19%) as a green-brownish solid. ^{1}H RMN (300 MHz, $CDCl_3$, 25ºC): 9.81-9.57 (8H, m, Ar-Pc), 8.86 (2H, d, *J* = 2.07 Hz, 2xH-TNF), 8.76 (2H, d, *J* = 2.20 Hz, 2xH-TNF), 8.73 (2H, d, *J* = 2.07 Hz, 2xH-TNF), 8.65 (2H, d, *J* = 2.20 Hz, 2xH-TNF), 8.50-8.42 (m, 4H, Ar-Pc), 6.22 (4H, d, *J* = 8.90 Hz, 4xH-Ar), 5.29 (4H, d, *J* = 8.90 Hz, 4xH-Ar), 4.44-4.32 (8H, m, 4xCO_2-CH_2), 3.67-3.57 (8H, m, 4xCO_2-CH_2-C*H*$_2$), 3.44-3.30 (16H, m, 8xCH_2-O), and 1.85-1.68 (36H, m, 4xC-$(CH_3)_3$) ppm. IR-FT (KBr) ν / cm^{-1}: 3082, 2956, 2907, 2866, 1736, 1617, 1592, 1466, 1342, 1283, 1228, 1156, 1110, 1084, 942, 759, 528. UV ($CHCl_3$), λ_{max} / nm (log ε): 257 (5.47), 329 (5.09), 358 (4.05), 426 (3.82), 625 (3.52), 664 (4.46) and 694 (5.26).
HR-MS (MALDI-TOF, DCTB): *m/z*= 3680.5920 [M$^+$]; calcd for $C_{232}H_{96}N_{14}O_{36}Si$: 3680.5875

Synthesis of SiPc 2:
A mixture of (^{t}Bu)$_4$SiPcCl_2[1] (290 mg, 0.347 mmol) and 4-hidroxybenzoic acid (400 mg, 2.9 mmol) in diglyme (10 ml) was stirred at 170ºC under argon atmosphere during 3 hours. After cooling the reaction mixture was diluted with AcOEt and washed with saturated $NaHCO_3$ solution. The solvent was then removed under reduced pressure and the product was purified by flash chromatography (SiO_2, $CHCl_3 \rightarrow CHCl_3$/ AcOEt 10:1) to yield compound **2** (19 mg, 5%) as a blue-greenish solid. ^{1}H RMN (300 MHz, DMSO-d_6, 25 ºC): 9.82-9.57 (8H, m, Pc), 9.42 (2H, s, 2x-OH), 8.68-8.54 (4H, m, Pc), 5.65 (4H, d, *J* = 8.70 Hz, 4xAr-H), 4.86 (4H, d, *J* = 8.70 Hz, 4xAr-H) and 1.83-1.60 (36H, m, 4xC-$(CH_3)_3$) ppm. IR-FT (KBr) ν / cm^{-1}: 3680-3095, 2963, 2904, 2868, 1678, 1608, 1591, 1529, 1512, 1484, 1412, 1325, 1283, 1260, 1161, 1080, 942 and 759. MS (MALDI-TOF, DCTB): 1038 (M$^+$). UV ($CHCl_3$), λ_{max} / nm (log ε): 297 (4.52), 361 (5.00), 623 (4.63), 663 (4.57) and 692 (5.45). HR-MS (MALDI-TOF, DCTB): *m/z*= 1308.4224. [M$^+$]; calcd for $C_{62}H_{58}N_8O_6Si$: 1308.4243.

Synthesis of TNF 5:
Tert-Butyl hemimalonate [2] (227 mg, 1.42 mmol), 11-hydroxy-3,6,9-trioxaundecyl-2,5,7-trinitrofluorenone-4-carboxylate[3] (613 mg, 1.15 mmol), DCC (586 mg, 2.84 mmol) and DMAP (96 mg, 0.79 mmol) in 20 mL of dry CH_2Cl_2, were stirred under argon atmosphere at 0ºC during 1 hour and at room temperature for 8 hours. A white solid was filtered off and the organic solution obtained was washed several times with saturated $NaHCO_3$ solution, HCl 1M and finally with brine. The solvent was then removed under reduced pressure and the product was purified by flash chromatography (SiO_2, Hexane/ AcOEt 1:1) to yield compound **5** (650 mg, 84%) as an orange oil. ^{1}H RMN (300 MHz, $CDCl_3$, 25ºC): 8.96 (1H, d, *J* = 2.06 Hz, H-TNF), 8.91 (1H, d, *J* = 2.22 Hz, H-TNF), 8.83 (1H, d, *J* = 2.06 Hz, H-TNF), 8.77 (1H, d, *J* = 2.22 Hz, H-TNF), 4.58-4.52 (2H, m, TNF-CO_2-CH_2), 4.29-4.24 (2H, m, C*H*$_2$- O_2C-CH_2), 3.91-3.86 (2H, m, TNF-CO_2-CH_2-C*H*$_2$), 3.76-3.63 (10H, m, 5 x CH_2-O) 3.30 (2H, s, CO-CH_2-CO), and 1.46 (9H, s, C-$(CH_3)_3$) ppm. ^{13}C RMN (75 MHz, $CDCl_3$, 25ºC): 184.9, 166.9, 165.5, 164.4,

[1] D. C. Gale and J. G. Gaudiello, *J. Am. Chem. Soc.* 1991, **113**, 1610.
[2] V. I. Tararov, A. Korostylev, G. König, A. Börner, *Synth. Commun.* 2006, **36**, 187.
[3] L. Martín-Gomis, F. Fernández-Lázaro, A. Sastre-Santos, J. A. Quintana, J. M. Villalvilla, P. Boj and M. A. Díaz-García, *Synth. Met.*, 2007, **157**, 1064-1070.

149.6, 149.3, 146.6, 143.5, 139.7, 138.8, 137.7, 132.1, 130.7, 125.2, 122.4, 121.8, 82.0, 70.5, 70.5, 68.8, 68.5, 66.1, 64.2, 53.4, 42.6 and 27.8 ppm. IR-FT (KBr) ν / cm^{-1}: 3092, 2877, 1739, 1617, 1595, 1539, 1456, 1346, 1313, 1234, 1143, 1043. MS (MALDI-TOF, DCTB): 700 (M +Na)$^+$. UV, λ_{max} / nm (log ε): 283 (4.37), 325 (3.90) and 350 (3.92).

Synthesis of TNF-C_{60} 6:

300 μL of DBU were added to a mixture of TNF malonate **5** (340 mg, 0.500 mmol), C_{60} (360 mg, 0.500 mmol) and iodine (200 mg, 0.79 mmol) in 300 mL of dry toluene,. The mixture was then stirred under argon atmosphere at room temperature during 24 hours. After the solvent was removed under reduced pressure, the crude material was purified twice by flash chromatography (first SiO_2, Toluene→Toluene/MeOH 20:1, and finally CH_2Cl_2→CH_2Cl_2/AcOEt 9:1) to afford the pure product as a brown solid (220 mg, 31%). ^{1}H RMN (300 MHz, $CDCl_3$, 25ºC): 8.95 (d, 1H, *J* = 2.08 Hz, H-TNF), 8.90 (d, 1H, *J* = 2.23 Hz, H-TNF), 8.82 (d, 1H, *J* = 2.08 Hz, H-TNF), 8.77 (d, 1H, *J* = 2.23 Hz, H-TNF), 4.64-4.59 (m, 2H, CH_2-O_2C-C<C_{60}), 4.58-4.52 (m, 2H, TNF-CO_2-CH_2), 3.92-3.85 (m, 4H, 2 x CO_2-CH_2-*CH_2*), 3.77-3.64 (m, 8H, 4 x CH_2-O and 1.68 (s, 9H, ^{t}Bu) ppm. ^{13}C RMN (75 MHz, $CDCl_3$, 25ºC): 184.8, 164.4, 163.8, 162.0, 149.6, 149.3, 146.6, 145.5, 145.3, 145.1, 145.1, 145.1, 144.7, 144.6, 144.5, 144.4, 143.8, 143.5, 143.0, 142.9, 142.8, 142.1, 142.1, 141.8, 141.7, 140.8, 140.7, 139.7, 139.0, 138.8, 137.7, 132.1, 130.7, 125.2, 122.4, 121.8, 85.1, 71.7, 70.6, 68.7, 68.6, 66.2, 65.9, 65.8, 53.0 and 28.0 ppm. IR-FT (KBr) ν / cm^{-1}: 3087, 2953, 2867, 1737, 1615, 1594, 1537, 1343, 1274, 1245, 1153, 1113, 1089 and 528. UV, λ_{max} / nm (log ε): 258 (5.13), 324 (4.63), 426 (3.34). MS (MALDI-TOF, dithranol): 1395 (M^+, 100)

Synthesis of TNF-C_{60} 3:

TNF-C_{60} derivative **6** (30 mg, 0.022 mmol) was stirred in 6 mL of a 5:1 CH_2Cl_2/ trifluoroacetic acid mixture at room temperature during 6 h. After the solvent was removed under reduced pressure, the crude material was washed several times with methanol to afford the pure product as a brown solid (25 mg, 87 %). ^{1}H RMN (300 MHz, $CDCl_3$, 25ºC): 8.99 (d, 1H, *J* = 2.14 Hz, H-TNF), 8.90 (d, 1H, *J* = 2.03 Hz, H-TNF), 8.76 (d, 1H, *J* = 2.03 Hz, H-TNF), 8.75 (d, 1H, *J* = 2.14 Hz, H-TNF), 4.65-4.60 (m, 2H, CH_2-O_2C-C<C_{60}), 4.60-4.55 (m, 2H, TNF-CO_2-CH_2), 4.06-4.00 (m, 2H, *CH_2*-CH_2-O_2C) and 3.95-3.72 (m, 10H, 5 x CH_2-O) ppm. ^{13}C RMN (75 MHz, $CDCl_3$, 25ºC): 184.8, 164.3, 163.4, 163.1, 149.7, 149.2, 146.4, 145.1, 145.0, 144.9, 144.7, 144.7, 144.5, 144.5, 144.4, 144.4, 144.3, 144.2, 143.6, 143.6, 143.6, 143.0, 142.9, 142.7, 142.0, 142.0, 141.7, 141.6, 140.6, 140.4, 139.7, 139.1, 138.8, 138.5, 137.7, 131.8, 131.1, 125.1, 122.3, 121.9, 71.4, 70.7, 70.6, 69.9, 68.6, 68.2, 65.8, 65.4 and 51.9 ppm. IR-FT (KBr) ν / cm^{-1}:3662-3184, 3089, 2869, 1737, 1615, 1592, 1537, 1343, 1312, 1277, 1233, 1178, 1115, 1089 and 528. UV ($CHCl_3$), λ_{max} / nm (logε): 258 (5.09), 325 (4.60) y 426 (3.47). MS (MALDI-TOF, dithranol, NaI): 1362 (M^++Na, 100) y 1339 (M^+, 51)

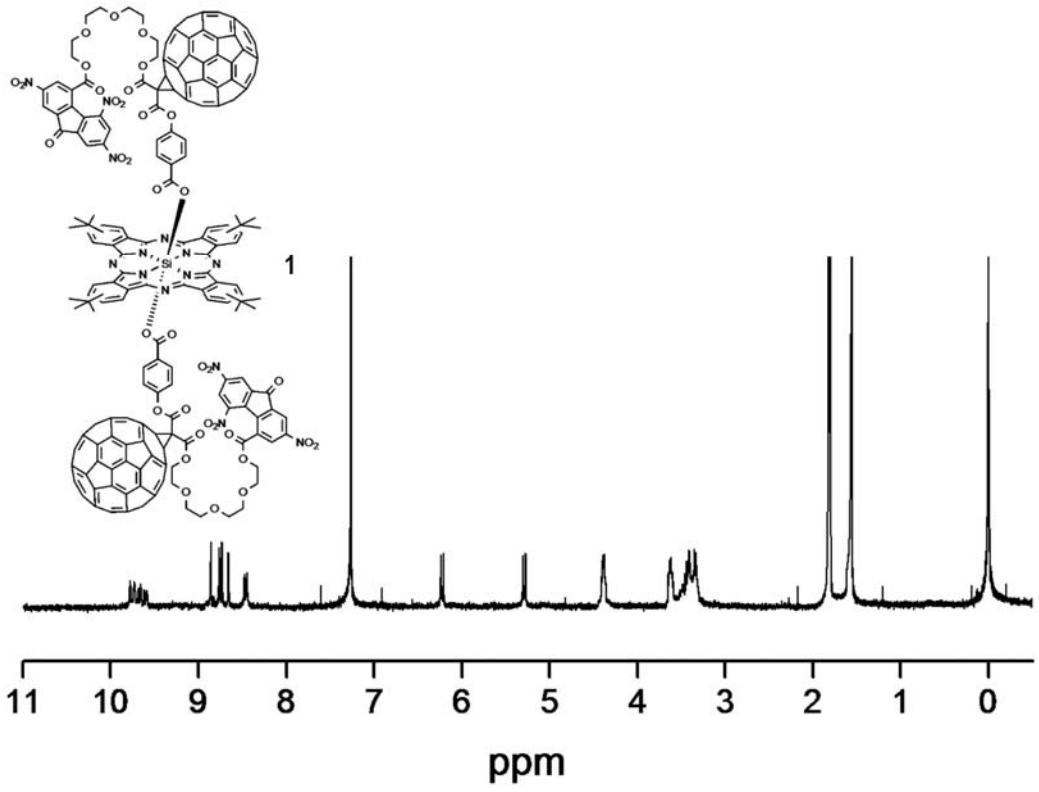


Figure S6. ^{1}H NMR spectrum of **1** in $CDCl_3$.

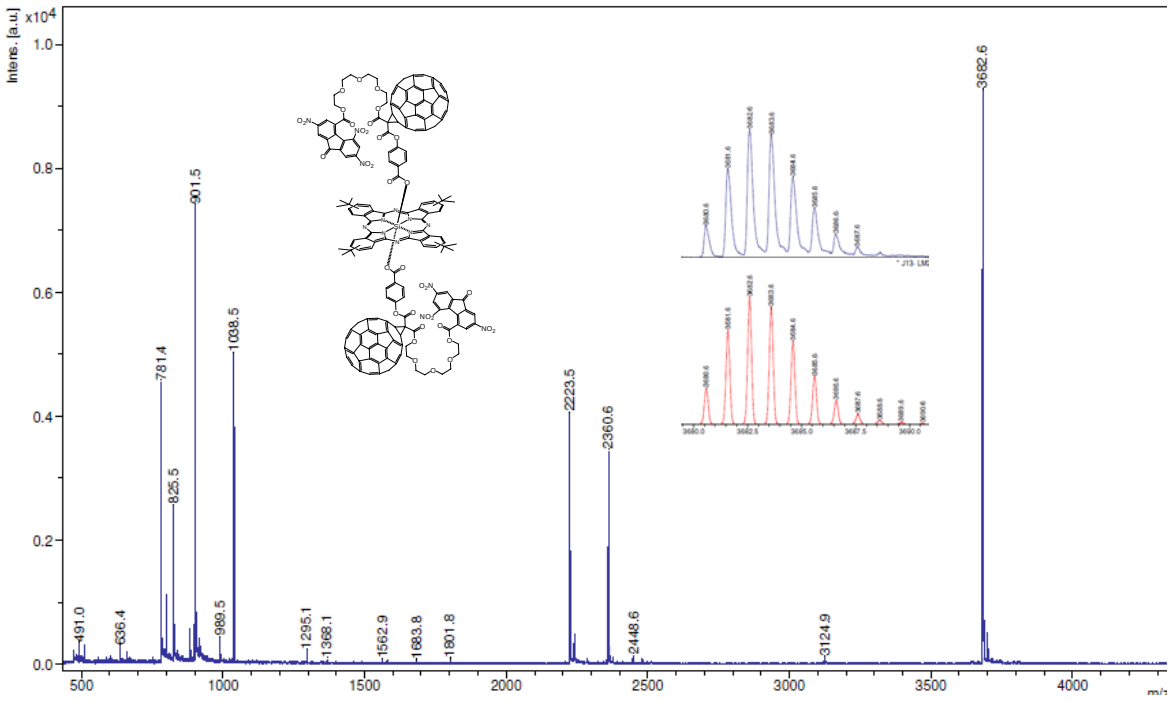


Figure S7a. MALDI-TOF mass spectrum of **1** (positive mode).

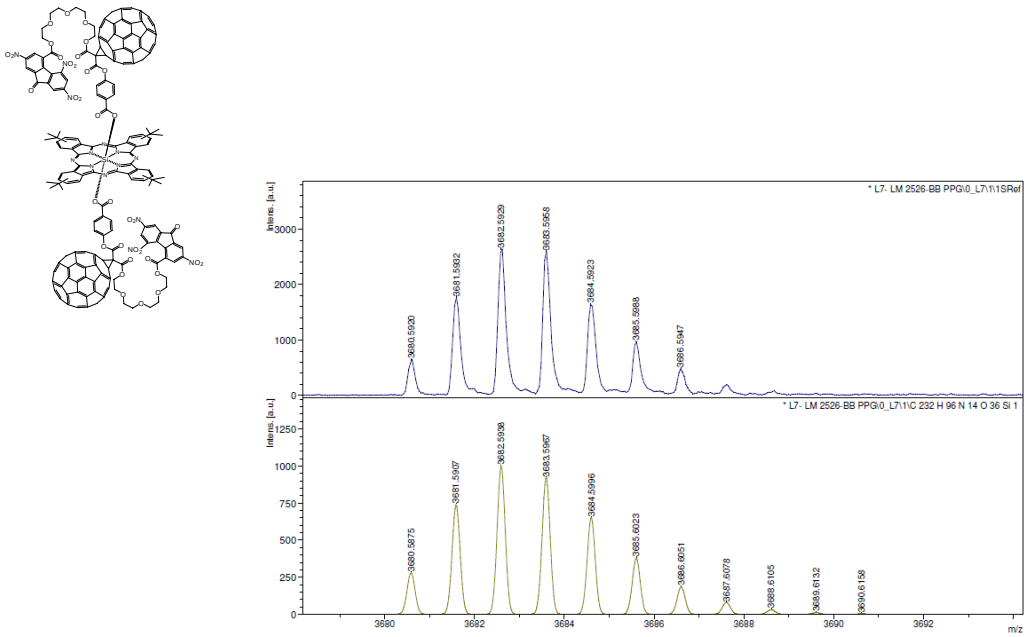


Figure S7b. High resolution MALDI-TOF mass spectrum of SiPc**1** ().

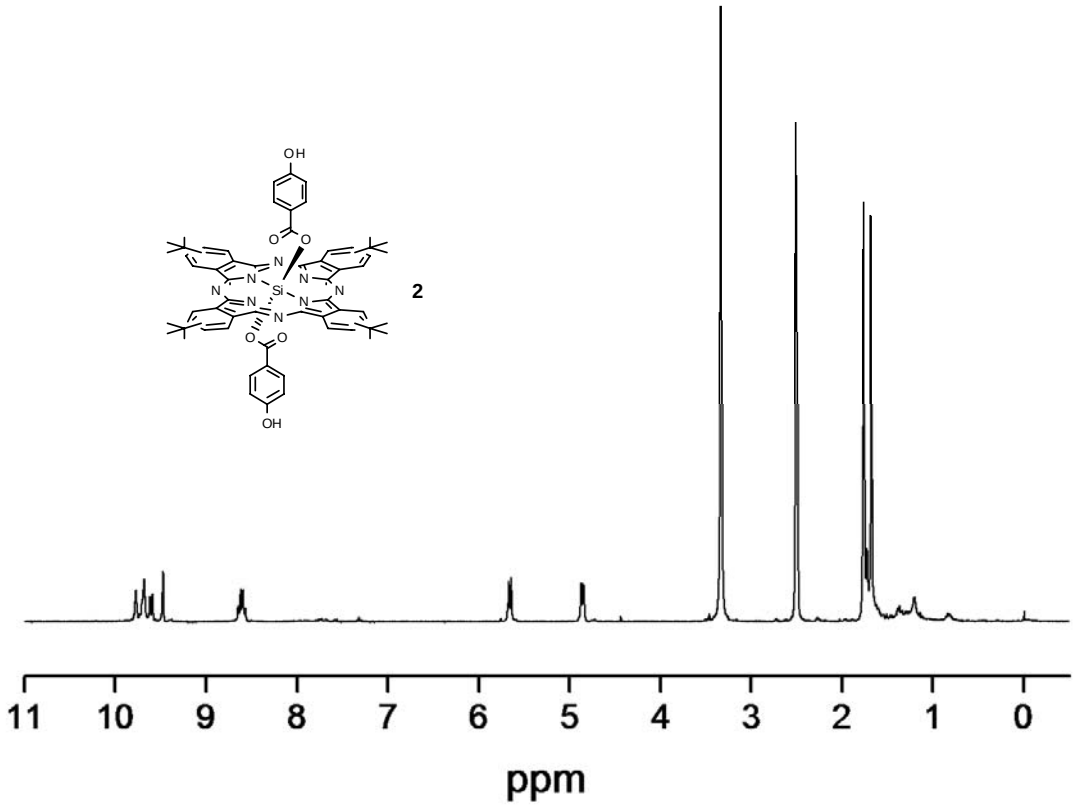


Figure S8a. ^{1}H NMR spectrum of SiPc **2** in DMSO-d_6.

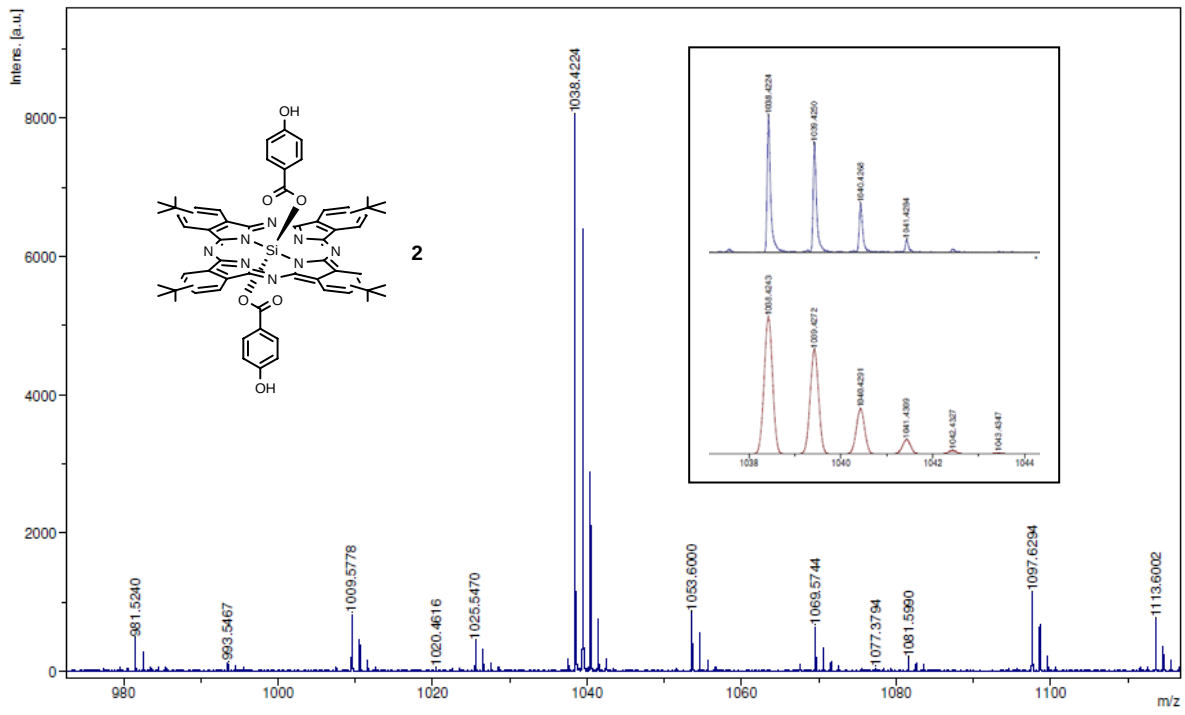


Figure S8b. High Resolution MALDI-TOF mass spectrum of SiPc **2** (positive mode).

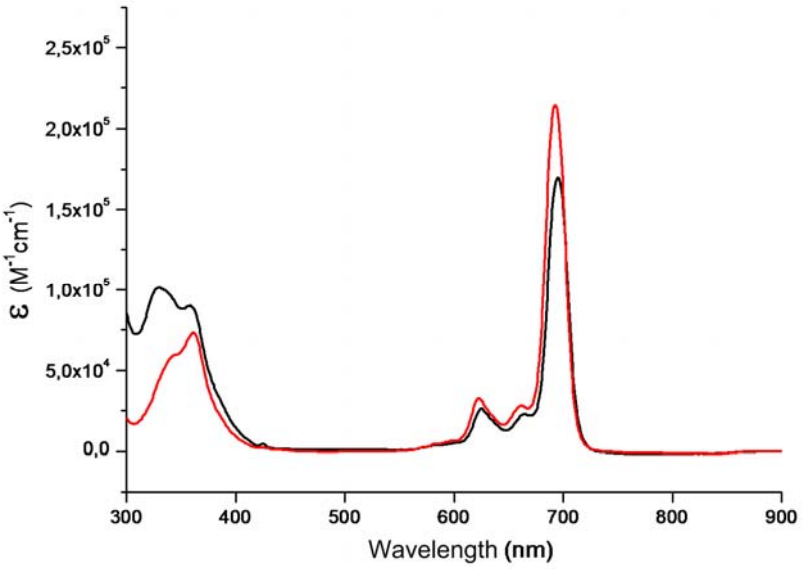


Figure S9. UV-vis spectra of pentad **1** (black line) and SiPc **2** (red line).

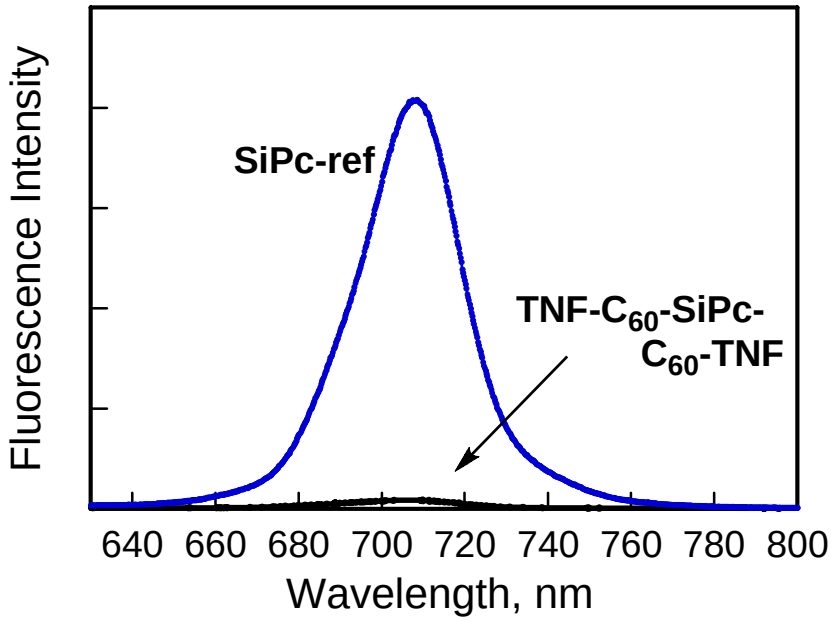
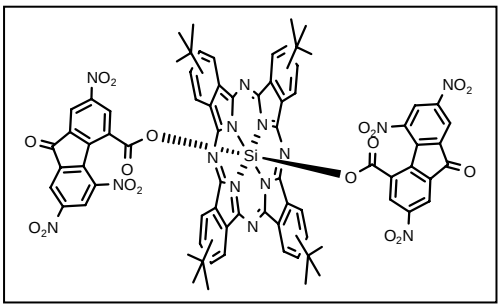
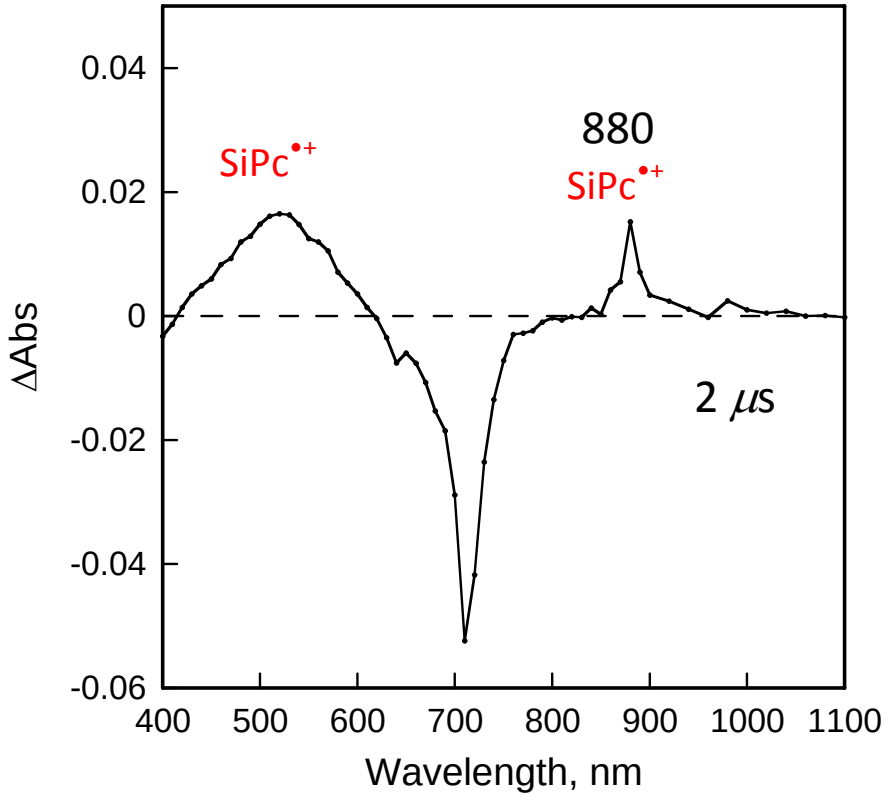


Fig. S10. Fluorescence spectra of SiPc-ref and TNF-C_{60}-SiPc-C_{60}-TNF in deaerated PhCN at 298 K. Excitation wavelength: 620 nm.



(a)



(b)

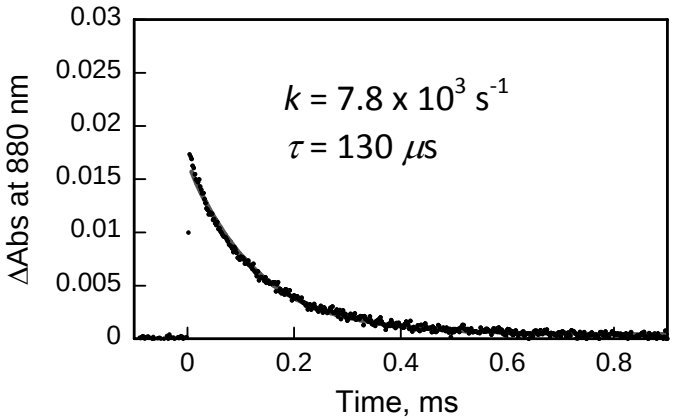


Figure S11. (a) Nanosecond transient absorption spectra of TNF-SiPc-TNF triad in deaerated PhCN at 298 K after laser excitation at 355 nm with $Mg(ClO_4)_2$ 10 mM. (b) Time profile of absorbance at 880 nm.