Electronic Supplementary Information

Switching the photo-induced energy and electron transfer processes in BODIPY-phthalocyanine conjugates

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Contents

Experimental Section

General. All the reactions were performed under an atmosphere of nitrogen. Tetrahydrofuran (THF), toluene and pyridine were distilled from sodium benzophenone ketyl, sodium and KOH respectively. Toluene used for photophysical measurements was of spectroscopic grade (Aldrich) and used without prior purification. All other solvents and reagents were of reagent grade and used as received. Chromatographic purifications were performed on silica gel (Macherey-Nagel, 70-230 mesh) columns with the indicated eluents.

^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX 300 (^{1}H, 300; ^{13}C, 75.4 MHz) or AVANCE II 400 (^{1}H, 400; ^{13}C, 100.6 MHz) spectrometer in $CDCl_3$. Spectra were referenced internally using the residual solvent (^{1}H: δ 7.26) or solvent (^{13}C: δ 77.0) resonances relative to $SiMe_4$. MALDI-TOF mass spectra were taken on a Bruker Daltonics Autoflex MALDI-TOF mass spectrometer. ESI mass spectra were measured on a Thermo Finnigan MAT 95 XL mass spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Photophysical studies. Ground-state absorption spectra were taken on a Cary 5G UV-Vis-NIR spectrophotometer. Steady-state fluorescence spectra were

measured using a combination of a cw-xenon lamp (XBO 150) and a monochromator (Lot-Oriel, bandwidth 10 nm) for excitation and a polychromator with a cooled CCD matrix as the detector system (Lot-Oriel, Instaspec IV).[1] Fluorescence quantum yields were determined by the equation: $\Phi_{F(sample)} = (F_{sample}/F_{ref})(A_{ref}/A_{sample})(n_{sample}^2/n_{ref}^2)\Phi_{F(ref)}$,[2] where F, A and n are the integrated fluorescence intensity, the absorbance at the excitation position and the refractive index of the solvent respectively. *meso*-Tetraphenylporphyrin in *N*,*N*-dimethylformamide (DMF) [$\Phi_{F(ref)} = 0.11$],[3] rhodamine 110 in ethanol [$\Phi_{F(ref)} = 0.94$][4] and rhodamine 6G in ethanol [$\Phi_{F(ref)} = 0.95$][5] were used as the references. Time-resolved fluorescence spectroscopic studies were carried out using the set-up described previously.[6]

To measure transient absorption spectra, a white light continuum was generated as a test beam in a cell with a D_2O/H_2O mixture using intense 25 ps pulses from a Nd^{3+}:YAG laser (PL 2143A, Ekspla) at 1064 nm. Before passing through the sample, the continuum radiation was split to obtain a reference spectrum. The transmitted as well as the reference beams were focused into two optical fibres and recorded simultaneously at different traces on a CCD-matrix (Lot-Oriel, Instaspec IV). Tunable radiation from an OPG/OPA (Ekspla PG 401/SH, tuning range 200-2300 nm) pumped by third harmonic of the same laser was used as an excitation beam. The

mechanical delay line allowed the measurement of light-induced changes of the absorption spectrum at different delays up to 15 ns after excitation. The OD of all samples was 1.0 at the maximum of the absorption band of lowest energy. The data were analysed using the compensation method.[7]

Electrochemical studies. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyser. The cell comprised inlets for a platinum-sphere working electrode, a platinum-plate counter electrode and a silver-wire pseudo-reference electrode. Typically, a 0.1 M solution of $[Bu_4N][PF_6]$ in DMF containing the sample was purged with nitrogen for 15 min, then the voltammograms were recorded at ambient temperature. Potentials were referenced to saturated calomel electrode (SCE) using ferrocene as an internal standard ($E_{1/2}$ = + 0.38 V *vs.* SCE).

Bis(BODIPY) substituted phthalocyanine 3. A mixture of BODIPY-appended phenol **1** (102 mg, 0.30 mmol), silicon(IV) phthalocyanine dichloride (**2**) (92 mg, 0.15 mmol) and a small amount of pyridine (0.5 mL) in toluene (15 mL) was refluxed for 48 h. The mixture was evaporated to dryness under reduced pressure, then the residue was chromatographed using $CHCl_3$ as the eluent. The second green fraction was collected and rotary evaporated. The crude product was further purified by recrystallisation from a mixture of CH_2Cl_2 and hexane to give

a gray-green solid (62 mg, 34%). ^{1}H NMR (300 MHz): δ 9.62-9.66 (m, 8 H, Pc-H$_\alpha$), 8.38-8.42 (m, 8 H, Pc-H$_\beta$), 5.70 (s, 4 H, pyrrole-H), 5.50 (d, J = 8.4 Hz, 4 H, p-C$_6$H$_4$), 2.60 (d, J = 8.4 Hz, 4 H, p-C$_6$H$_4$), 2.34 (s, 12 H, CH$_3$), 0.57 (s, 12 H, CH$_3$); ^{13}C{^{1}H} NMR (75.4 MHz): δ 154.7, 150.1, 149.7, 142.8, 141.5, 135.4, 131.5, 131.0, 127.0, 125.6, 123.9, 120.6, 118.4, 14.3, 14.2; MS (MALDI-TOF): several isotopic clusters peaking at m/z 1218 {8%, [M]$^+$}, 1200 {24%, [M-F+H]$^+$} and 880 {100%, [M–BODIPY]$^+$}; HRMS (MALDI-TOF): m/z calcd for $C_{70}H_{52}B_2F_4N_{12}O_2Si$ [M]$^+$: 1218.4243, found: 1218.4265. Anal. Calcd for $C_{70}H_{52}B_2F_4N_{12}O_2Si$: C, 68.97; H, 4.30; N, 13.79. Found: C, 68.69; H, 4.77; N, 13.75.

Mono-styryl BODIPY 5. A mixture of BODIPY-appended phenol **1** (0.34 g, 1.0 mmol), 3,4,5-trimethoxybenzaldehyde (**4**) (0.20 g, 1.0 mmol), glacial acetic acid (2.0 mL, 34.9 mmol), piperidine (2.4 mL, 24.3 mmol) and a small amount of $Mg(ClO_4)_2$ in toluene (60 mL) was refluxed for 10 h. The water formed during the reaction was removed azeotropically with a Dean-Stark apparatus. The mixture was concentrated under reduced pressure, then the residue was purified by column chromatography using ethyl acetate/CH_2Cl_2 (1:25 v/v) as the eluent. The pink fraction was collected and rotary evaporated to yield the desired product **5** (0.12 g, 23 %). ^{1}H NMR (300 MHz): δ 7.55 (d, J = 16.2 Hz, 1 H, CH=CH), 7.16 (d, J = 8.4 Hz, 2 H, p-C$_6$H$_4$), 7.15 (d, J = 16.2 Hz, 1 H, CH=CH), 6.97 (d, J = 8.4 Hz, 2 H, p-C$_6$H$_4$), 6.80

(s, 2 H, ArH), 6.59 (s, 1 H, pyrrole-H), 6.02 (s, 1 H, pyrrole-H), 5.21 (s, 1 H, OH), 3.94 (s, 6 H, OCH_3), 3.89 (s, 3 H, OCH_3), 2.60 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3); $^{13}C\{^1H\}$ NMR (100.6 MHz): δ 156.3, 155.4, 153.4, 152.4, 143.0, 142.4, 140.4, 139.1, 136.0, 133.2, 132.3, 129.6, 127.2, 121.3, 118.6, 117.5, 116.1, 104.6, 61.0, 56.2, 14.8, 14.7, 14.6 (two of the aromatic signals are overlapped); HRMS (MALDI-TOF): *m/z* calcd for $C_{29}H_{29}BF_2N_2NaO_4$ $[M+Na]^+$: 541.2086, found: 541.2104.

Bis(mono-styryl BODIPY) substituted phthalocyanine 6. According to the procedure for the preparation of **3**, the mono-styryl BODIPY **5** (104 mg, 0.20 mmol) was treated with silicon(IV) phthalocyanine dichloride (**2**) (62 mg, 0.10 mmol) to give **6** as a purple solid (33 mg, 21%). ^1H NMR (300 MHz): δ 9.64-9.67 (m, 8 H, Pc-H_α), 8.39-8.43 (m, 8 H, Pc-H_β), 7.33 (d, J = 16.2 Hz, 2 H, CH=CH), 6.98 (d, J = 16.2 Hz, 2 H, CH=CH), 6.68 (s, 4 H, ArH), 6.31 (s, 2 H, pyrrole-H), 5.75 (s, 2 H, pyrrole-H), 5.53 (d, J = 8.4 Hz, 4 H, *p*-C_6H_4), 3.87 (s, 12 H, OCH_3), 3.84 (s, 6 H, OCH_3), 2.63 (d, J = 8.4 Hz, 4 H, *p*-C_6H_4), 2.39 (s, 6 H, CH_3), 0.61 (s, 6 H, CH_3), 0.60 (s, 6 H, CH_3); $^{13}C\{^1H\}$ NMR (75.4 MHz): δ 154.8, 153.3, 151.9, 150.1, 149.7, 142.6, 142.0, 140.2, 139.0, 135.6, 135.4, 132.4, 132.2, 131.5, 127.2, 125.7, 123.9, 120.8, 118.3, 116.9, 104.5, 60.9, 56.2, 14.5, 14.4, 14.2 (some of the signals are overlapped); MS (ESI): two isotopic clusters peaking at *m*/z 1598 {42%, $[M+Na]^+$} and 1057 {100%, [M-

mono-styryl BODIPY]$^+$}; HRMS (ESI): *m*/*z* calcd for $C_{90}H_{72}B_2F_4N_{12}NaO_8Si$ $[M+Na]^+$: 1597.5380, found: 1597.5378.

SiPc(OC$_6$H$_4$CO$_2$CH$_3$)$_2$ (7). According to the procedure for the preparation of **3**, silicon(IV) phthalocyanine dichloride (**2**) (61 mg, 0.10 mmol) was treated with methyl 4-hydroxybenzoate (61 mg, 0.40 mmol) to give **7** as a blue solid (45 mg, 53%). ^{1}H NMR (300 MHz): δ 9.61-9.68 (m, 8 H, Pc-H$_\alpha$), 8.37-8.42 (m, 8 H, Pc-H$_\beta$), 6.30 (d, J = 7.8 Hz, 4 H, *p*-C$_6$H$_4$), 3.43 (s, 6 H, OCH$_3$), 2.45 (d, J = 7.8 Hz, 4 H, *p*-C$_6$H$_4$); ^{13}C{^{1}H} NMR (75.4 MHz): δ 154.0, 149.6, 135.3, 131.4, 129.2, 123.9, 120.9, 117.3, 51.3 (the carbonyl signal was too weak to be observed); MS (MALDI-TOF): an isotopic cluster peaking at *m*/z 843 {27%, $[M+H]^+$}; HRMS (MALDI-TOF): *m*/*z* calcd for $C_{48}H_{31}N_8O_6Si$ $[M+H]^+$: 843.2130, found: 843.2143.

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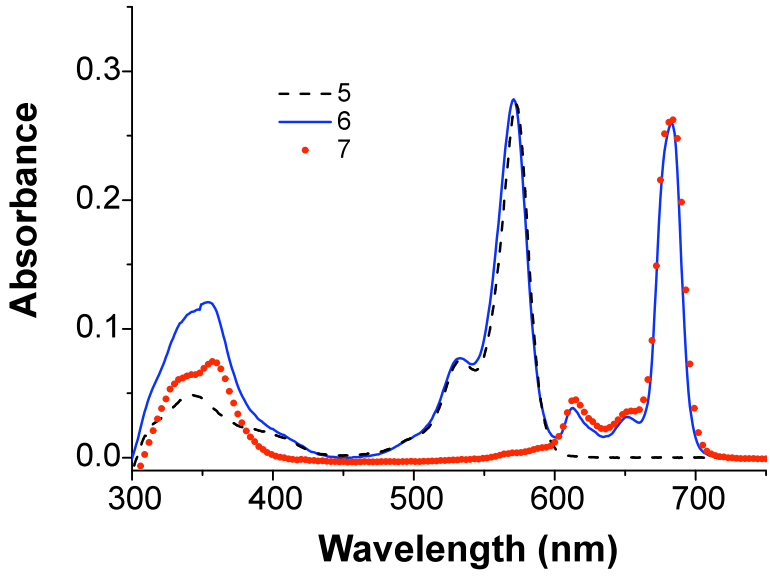


Fig. S1 Normalised absorption spectra of **5**-**7** in toluene. The spectra of **5** and **6** were normalised at 573 nm, while those of **6** and **7** were normalised at 683 nm.

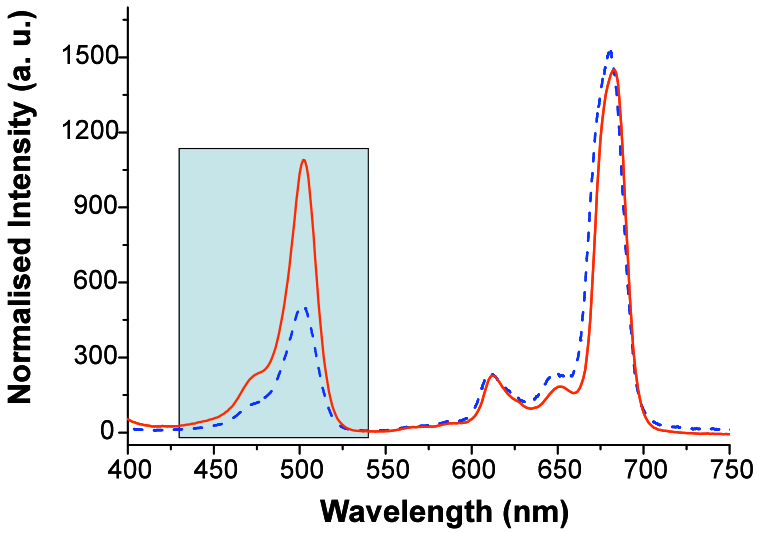


Fig. S2 Normalised (at 613 nm) absorption (—) and excitation (---) (monitored at 687 nm) spectra of **3** in toluene.

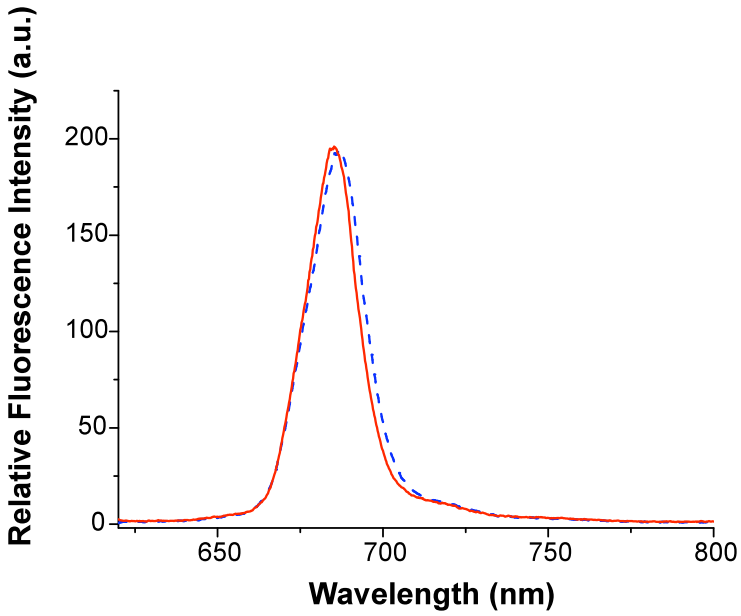


Fig. S3 Fluorescence spectra of **3** (—) and **7** (---) at equal absorbance at 613 nm in toluene (λ_{ex} = 613 nm).

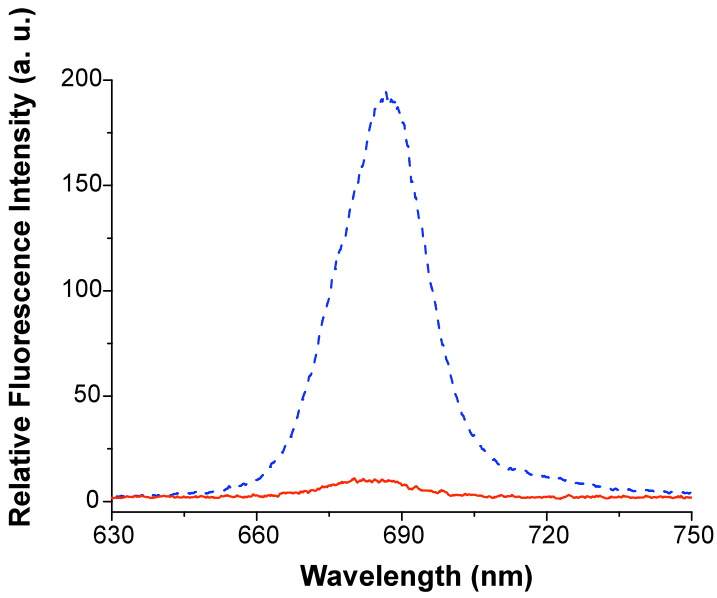
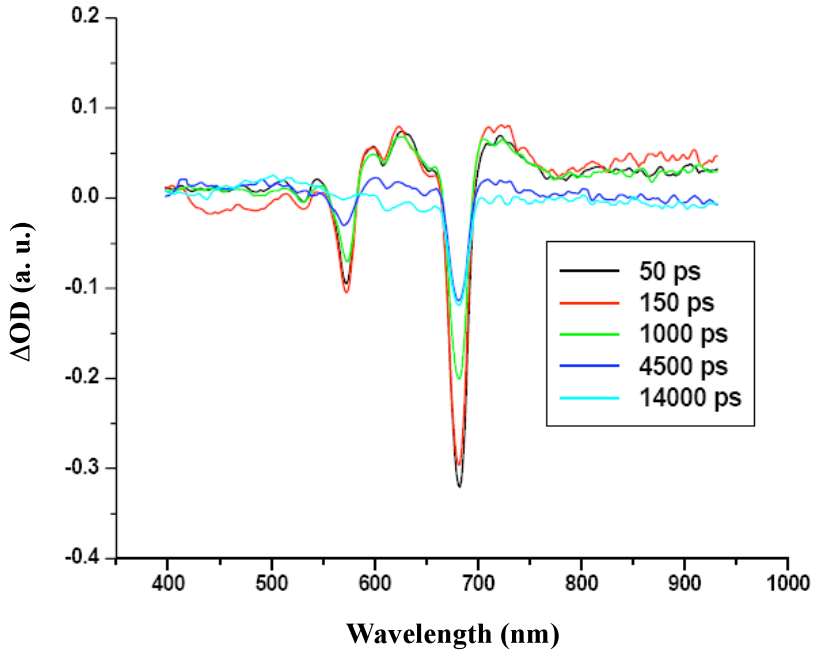


Fig. S4 Fluorescence spectra of **6** (—) and **7** (---) at equal absorbance at 613 nm in toluene (λ_{ex} = 613 nm).

(a)



(b)

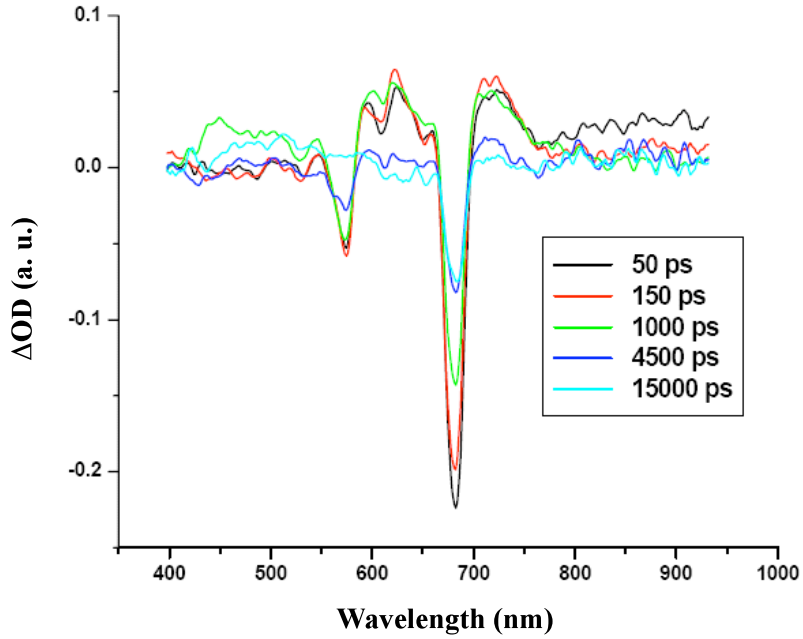
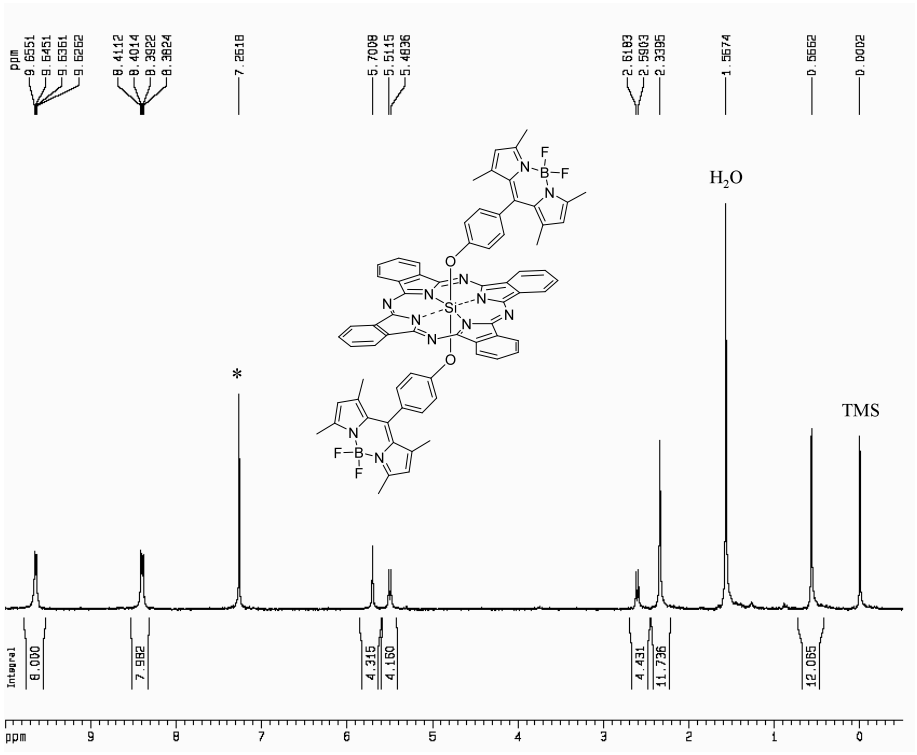
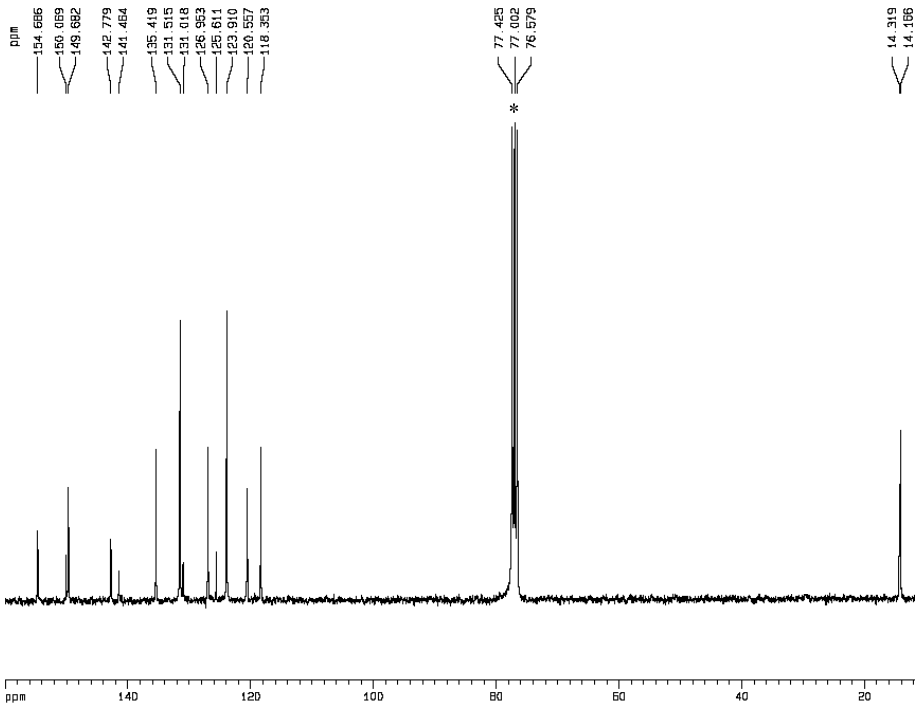


Fig. S5 Transient absorption spectra of **6** in toluene at different delay times. The excitation was made at (a) 530 nm and (b) 615 nm.

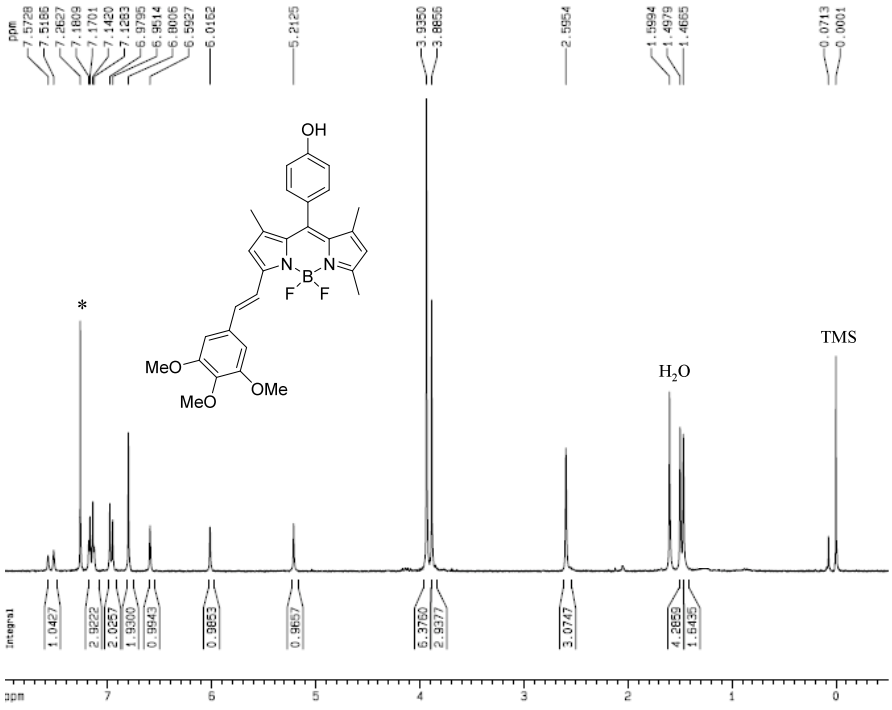
In all of the following spectra, (residual) solvent signals are marked with asterisks.



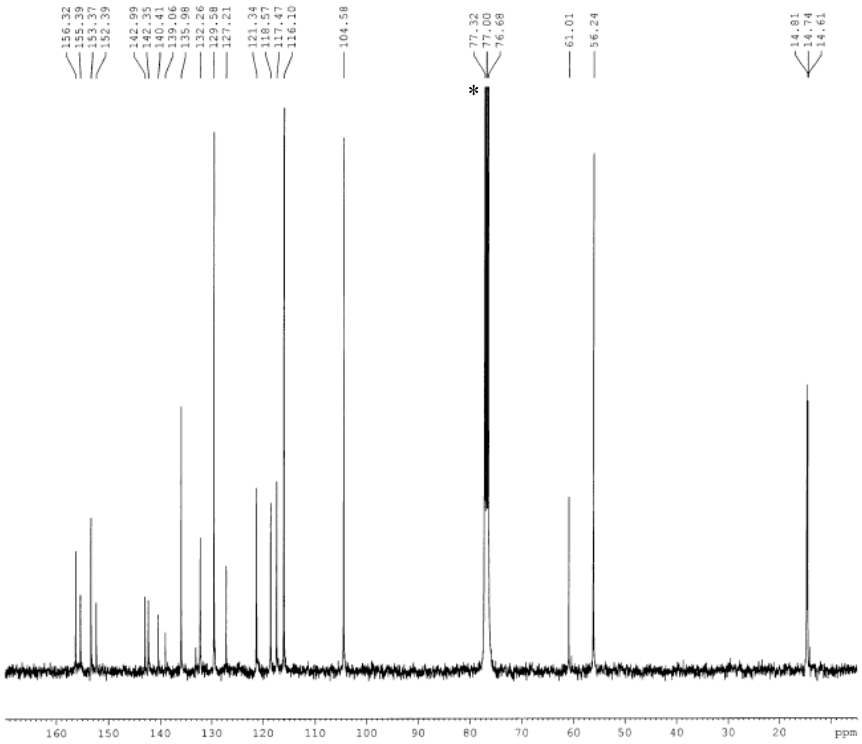
^{1}H NMR spectrum of compound **3** in $CDCl_3$



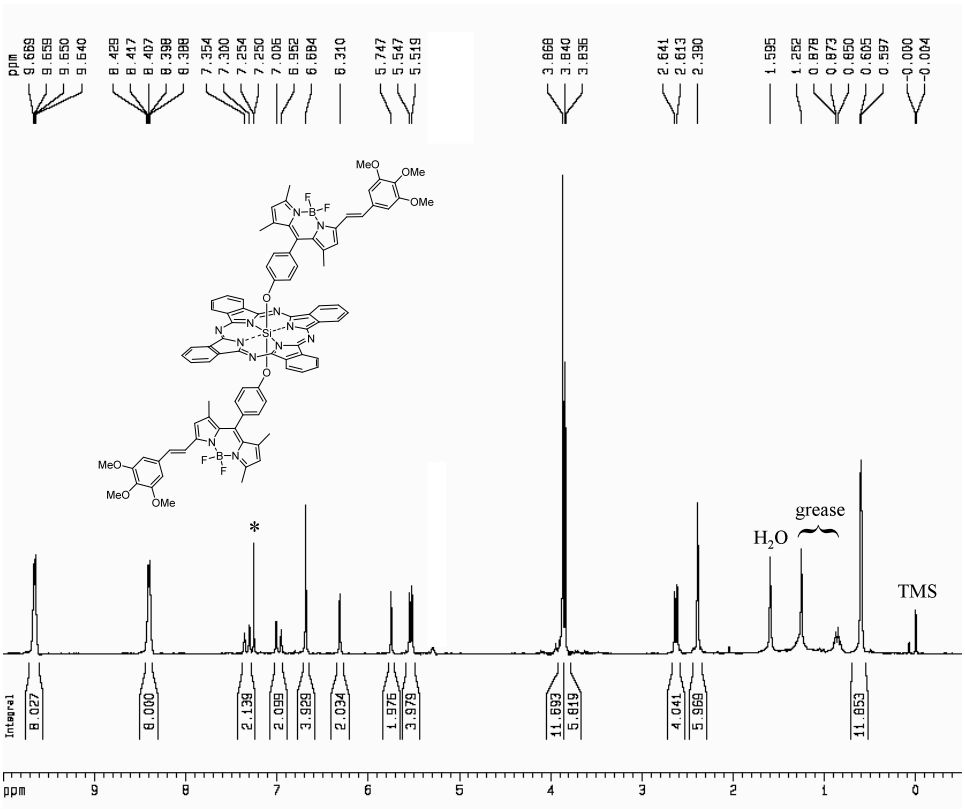
^{13}C{^{1}H} NMR spectrum of compound **3** in $CDCl_3$



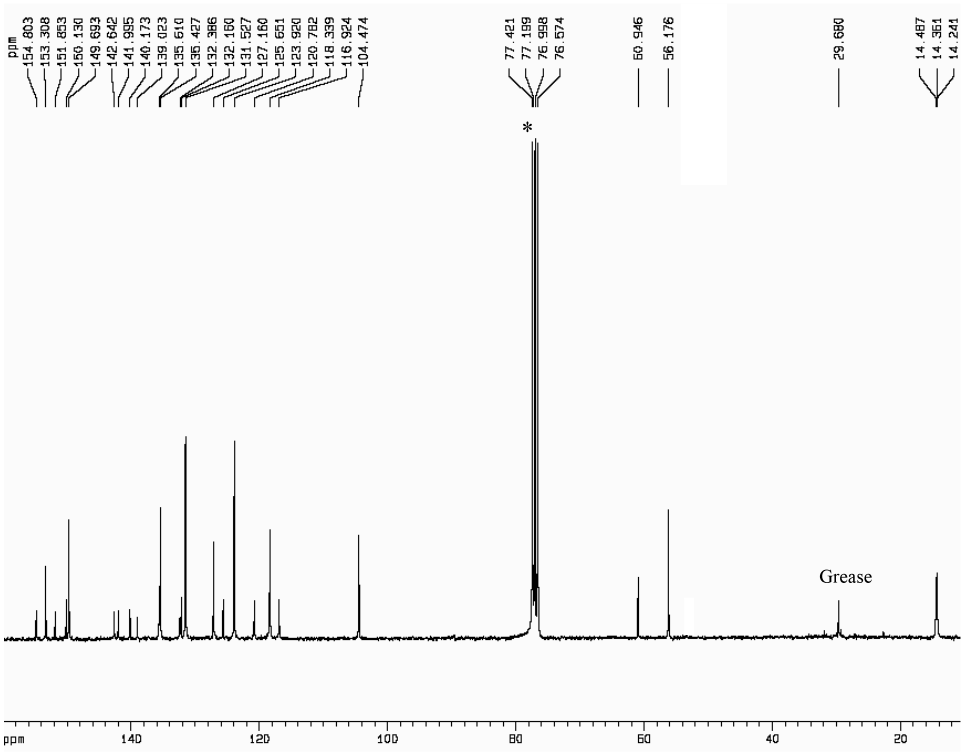
^{1}H NMR spectrum of compound **5** in $CDCl_3$



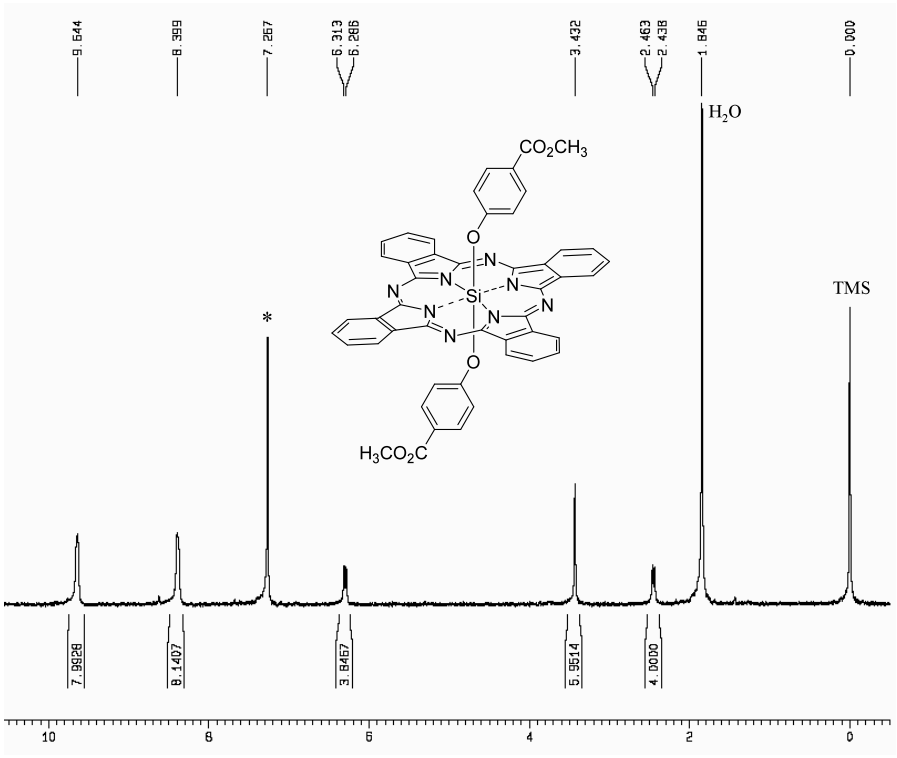
$^{13}C\{^{1}H\}$ NMR spectrum of compound **5** in $CDCl_3$



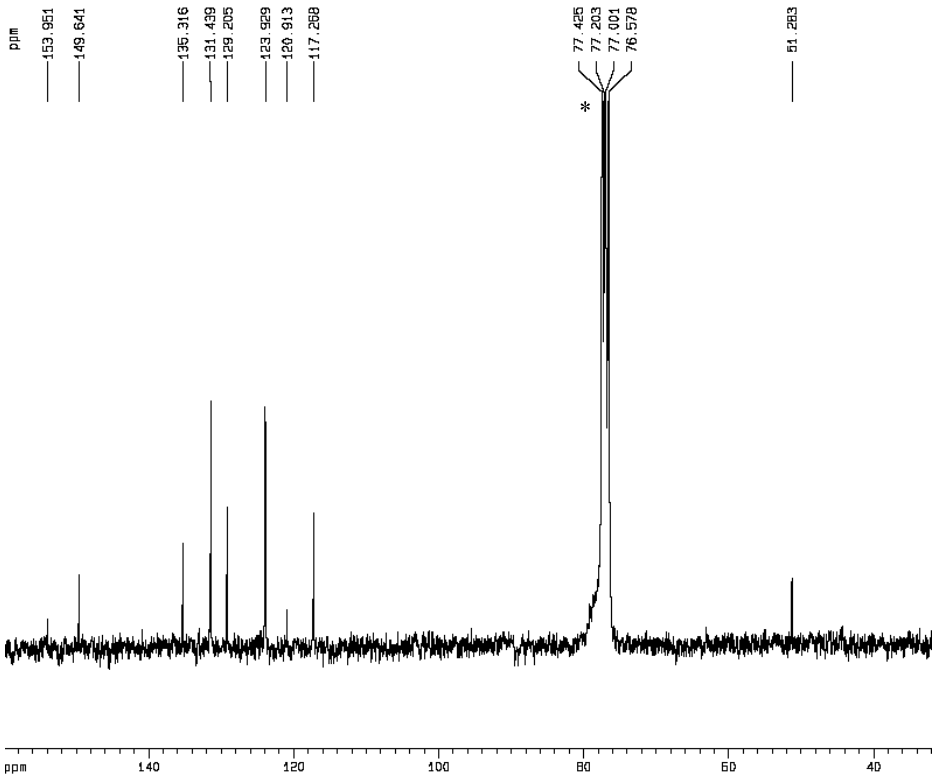
^{1}H NMR spectrum of compound **6** in $CDCl_3$



$^{13}C\{^{1}H\}$ NMR spectrum of compound **6** in $CDCl_3$



^{1}H NMR spectrum of compound **7** in $CDCl_3$



^{13}C{^{1}H} NMR spectrum of compound **7** in $CDCl_3$