Electronic Supplementary Material (ESI) for Journal of Materials Chemistry
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Electronic Supplementary Information (ESI†)

Energy Transfer Cassettes Based on Coumarin–Bodipy/Distyryl Bodipys Dyads

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1. Materials and general methods

All reagents were purchased from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. Twice-distilled water was used throughout all experiments. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Qingdao Yuminyuan Chemicals GF254 silica gel coated plates. Flash chromatography (FC) was carried out using silica gel (200–300 mesh), obtained from the Qingdao Ocean Chemicals. Absorption spectra were taken on Agilent 8453 UV–vis spectroscopy system using a 1-cm quartz cell. Fluorescence spectra were taken on an Edinburgh Analytical Instruments (FL/FS 900). The ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75MHz, respectively. The following abbreviations were used to explain the multiplicities: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad. High resolution mass spectra were obtained on a Varian QFT-ESI mass spectrometer.

2. Determination of Quantum Yields

Steady-state fluorescence spectroscopic studies were performed on an Edinburgh Analytical Instruments (FL/FS 900). The slit width was 1 nm for both excitation and

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emission. The relative quantum yields of the samples were obtained by comparing the area under the corrected emission spectrum of the test sample with that of a standard. Fluorescein[1] in 0.1 N NaOH aqueous solution ($\Phi_f = 0.79$) and Rhodamine B[2] in EtOH ($\Phi_f = 0.70$) were used as the standard for the fluorescent quantum yield calculation according to the absorption of the test sample. Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions ($0.01<A<0.05$) were used to minimize the reabsorption effects. The quantum yield of fluorescence were measured three times for each dye and averaged. Quantum yields were determined using the following equation: [3,4]

$$\mathbf{\Phi_x = \Phi_{st} (I_x / I_{st}) (A_{st} / A_x) (\eta_x^2/\eta_{st}^2)}$$

Where Φ_{st} is the reported quantum yield of the standard, I is the area under the emission spectra, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent used. The X subscript denotes unknown, and st denotes standard. Molar extinction coefficients were obtained from the slope of a graph of absorbance *vs* concentration for each dye with five different concentrations (10^{-6} M).

3. Calculation Details. To understand the molecular geometry it was assigned that the phenyl bridge is not planar in the ground state or the excited state, geometry optimization of cassette **5** was performed to confirm such conclusion. The ground state structural optimization of cassette **5** was calculated with density functional theory (DFT) at the B3LYP/6-31G* level using Gaussian 03.[6] The geometric of the relevant excited states was optimized by taking advantage of the restricted single excited configuration interaction approach (CIS).

4. Synthesis

*4.1 Compound **3** and **4***

3-(4-Methylphenyl)-coumarin **(3)** and 3-(4-Formylphenyl)-coumarin **(4)** were prepared according to the reported procedure.[5]

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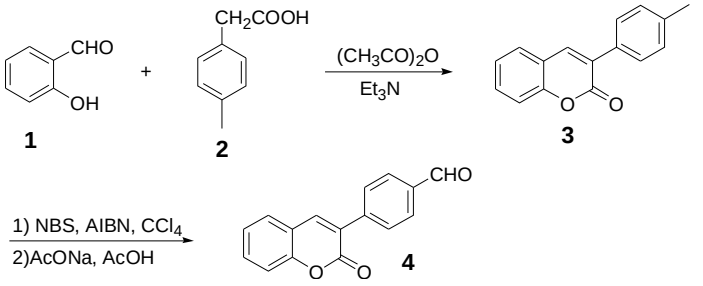

2-hydroxybenzaldehyde (**1**, 6.6g, 54 mmol), 4-methylphenylacetic acid (**2**, 7.8 g, 51 mmol), and acetic anhydride (27.4 mL, 0.29 mol) were placed in a 100 ml round-bottom flask. Triethylamine (9.3 mL, 23 mmol) was then added via the addition funnel over 8 min, and the reaction mixture was heated to reflux for 12 h. After the reaction, water (20 ml) was poured and the resulting yellow solid was collected by filtration. The solid was washed with water and ethanol, recrystallized from ethanol, and dried at vacuum overnight to afford **3** as an off-white solid. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.75 (s, 1H), 7.59 (d, J = 7.8 Hz, 2H), 7.51–7.22 (m, 6H), 2.37 (s, 3H).

To a solution of compound **3** (4.0 g, 17.0 mmol) in 250 mL of CCl_4 was added NBS (7.6 g, 42.5 mmol) and a trace amount of AIBN, and the mixture was then refluxed. After reaction for 8 h, the solvent was removed under reduced pressure. To the resulting residue were added NaOAc (8.4 g, 101.9 mmol) and acetic acid (100 mL), and the mixture was heated to reflux for 12 h. Subsequently, 2 N HCl (50 mL) was added to the hot reaction mixture, and the reaction was allowed to continue for 30 min. The reaction mixture was then evaporated to dryness, and the residue was purified by chromatography on silica gel (CH_2Cl_2: petroleum ether = 3:1) to afford **4** as a colorless powder (2.7 g, yield 65%): ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 10.0 (s, 1H), 7. 98–7.89 (m, 5H), 7.57–7.61 (m, 2H), 7.26–7.42 (m, 2H).

*4.2 Compound **5***

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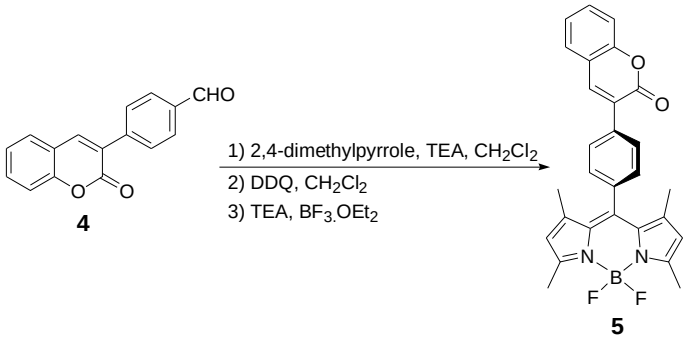
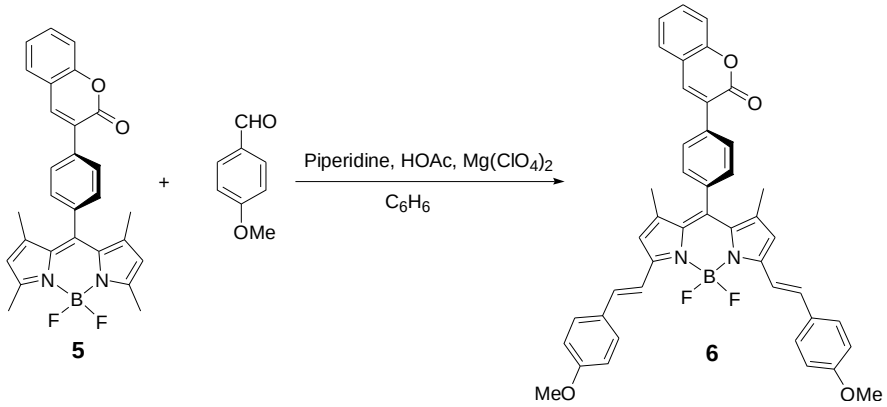


2,4-dimethylpyrrole (760 mg, 8.0 mmol) and 3-(4-formylphenyl)-coumarin (**4**) (1.0g, 4.0 mmol) were dissolved in 400 ml absolute CH_2Cl_2 under N_2 atmosphere. One drop of TFA was added and the solution stirred at r.t. until TLC-control showed the complete consumption of the aldehyde. At this point, a solution of tetrachlorobenzoquinone (DDQ, 0.986g, 4.0 mmol) in 100 mL absolute CH_2Cl_2 was added, stirring was continued for 1 h followed by the addition of 6 mL of Et_3N and 6 mL of $BF_3 \cdot OEt_2$ respectively. After stirring for 1h the reaction mixture was washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was chromatographed on silica gel (CH_2Cl_2: petroleum ether = 4:1) to afford 0.85 g **5** as orange needles. Yield: 48 %. ^{1}H NMR (300 MHz, CDCl3): δ 7.96 (s, 1H), 7.91(d, J = 8.1 Hz, 2H),7.58 (t, J = 7.8 Hz, 2H), 7.42–7.33 (m, 3H), 6.00 (s, 2H), 5.30 (s, 1H), 2.56 (s, 6H), 1.45 (s, 6H); ^{13}C NMR (75 MHz, CDCl3) 156.5, 154.5, 143.7, 141.2, 136.4, 132.7, 129.0, 125.5, 122.2, 120.3, 117.4, 15.5; HRMS calcd for (M + Na^+) 491.1713, found 491.1720.

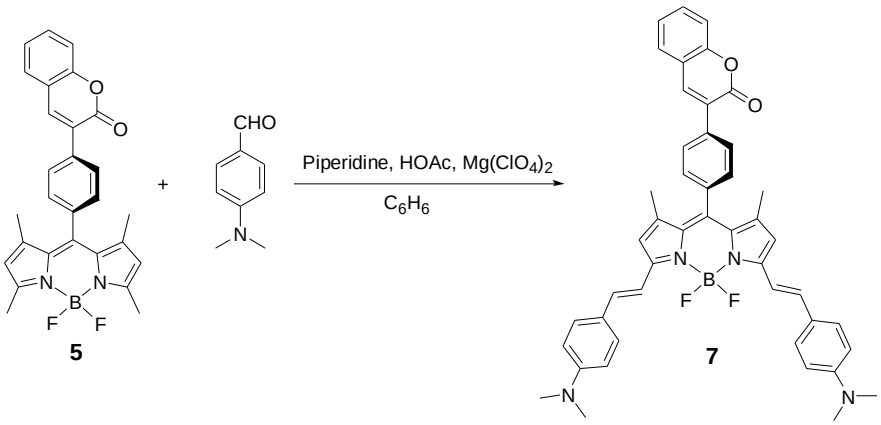
*4.3 Compound **6***



Compound **5** (0.31 g, 0.66 mmol) and 4-Methoxybenzaldehyde (0.269 g, 1.98 mmol) were refluxed in a mixture of toluene (50 mL), glacial acetic acid (0.5 mL), piperidine

(0.6 mL) and small amount of $Mg(ClO_4)_2$. Any water formed during the reaction was removed azeotropically by heating overnight in a Dean-Stark apparatus. Crude product concentrated under vacuum, then purified by silica gel column chromatography (CH_2Cl_2: petroleum ether = 2:3). The green colored fraction was collected and the solvent was removed under reduced pressure to yield the desired material **6** (0.30 g, 62.5 %). ^{1}H NMR(300 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.88 (d, *J* = 6.78 Hz, 2H), 7.63-7.53 (m, 8H), 7.40 (m, 3H), 7.30 (m, 1H), 7.17 (s, 1H), 6.91 (d, *J* = 8.7 Hz ,4H), 6.61 (s, 1H), 3.84 (s, 6H), 1.48(s, 6H); ^{13}C NMR(75 MHz, $CDCl_3$): δ 161.1, 153.5, 142.3, 142.0, 137.9, 136.6, 136.0, 133.7, 132.4, 130.1, 129.7, 129.4, 128.7, 125.3, 118.3, 117.8, 117.2, 114.9, 56.1, 15.6; HRMS calcd for $(M)^+$ 704.2658, found 704.2653.

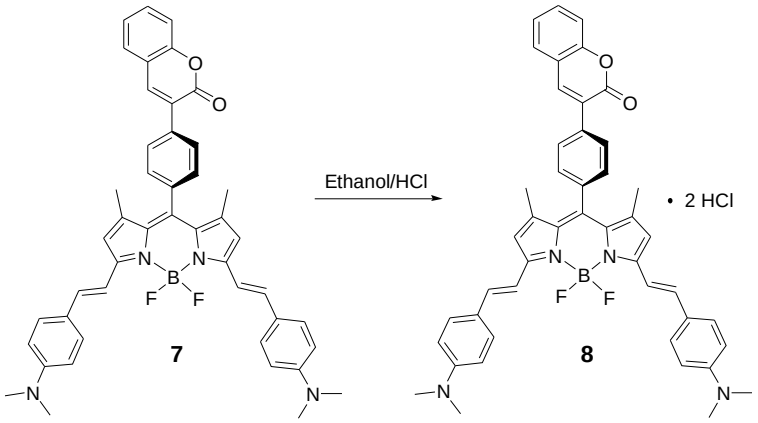
*4.4 Compound **7***



Compound **5** (0.31g, 0.66 mmol) and dimethylaminobenzaldehyde (0.294 g, 1.32 mmol) were refluxed in a mixture of toluene (50 mL), glacial acetic acid (0.5 mL), piperidine (0.6 mL) and small amount of $Mg(ClO_4)_2$. Any water formed during the reaction, was removed azeotropically by heating overnight in a Dean-Stark apparatus. Crude product concentrated under vacuum, then purified by silica gel column chromatography (CH_2Cl_2: petroleum ether=1:3→2:3). The green colored fraction was collected and the solvent was removed under reduced pressure to yield the desired material **7** (0.28 g, 46.67 %). ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6): δ 8.33 (s, 1H), 8.14 (s, 2H), 7.97 (s, 2H), 7.78 (s, 1H), 7.66 (m, 2H), 7.48-7.73 (m, 11H), 6.76 (s, 6H), 3.04 (s, 12H), 1.50 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): 160.2, 153.6, 140.2, 135.4, 131.7, 129.1, 128.8, 128.0, 127.3, 124.6, 119.5, 117.8, 116.5, 29.6, 14.8. HRMS [ESI]:

m/z, calcd for ($M+Na^+$) 753.3183, Found 753.3187.

*4.5 Compound **8***



The compound **8** is the doubly protonated species of **7**, and could easily prepared by treatment of ethanol solution of **7** with excess ethanol-HCl, followed by evaporation to dryness. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.81 (d, *J* = 6.0 Hz, 2H), 8.47 (m, 1H), 7.94–7.98 (m, 5H), 7.72–7.83 (m, 9H), 7.56–7.61 (m, 2H), 7.20–7.45 (m, 4H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.21 (s, 12H), 1.25 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 152.4, 143.2, 141.3, 133.9, 132.2, 129.4, 128.7, 125.1, 121.4, 118.6, 46.7, 15.3. HRMS [ESI]: *m/z*, calcd for (M–2HCl) 730.3285, Found 730.3282.

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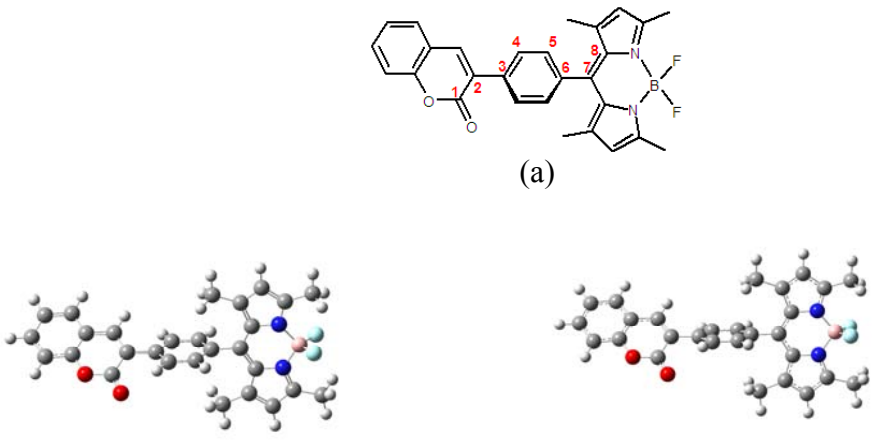

Fig. S1 (a) Chemical structure of cassette **5**. (b) The optimized geometry of cassette **5** in ground state. The dihedral angles of C1C2C3C4 and C5C6C7C8 are 144.85° and 89.33°, respectively. (c) The optimized geometry of cassette **5** in the first excited state. The dihedral angle of C1C2C3C4 and C5C6C7C8 are 135.45° and 89.09°, respectively.

(1) Lager, E., J. Z. Liu, et al., *J. Org. Chem.*, 2009, **74**, 2053–2058.

(2) Hu, R. R., E. Lager, et al., *J. Phys. Chem. C*, 2009, **113**, 15845–15853.

(3) Parker, C. A.; Rees, W. T., *Analyst*, 1962, **87**, 83–111.

(4) Williams, A. T. R.; Winfield, S. A.; Miller, J. N., *Analyst*, 1983, **108**, 1067–1071.

(5) W. Lin, L. Yuan, Z. Cao, Y. Feng, J. Song, *Angew. Chem. Int. Ed.*, 2010, **49**, 375.

(6) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *GAUSSIAN 03* (Revision D.02), Gaussian, Inc., Wallingford CT, 2004.

5. Spectroscopic data

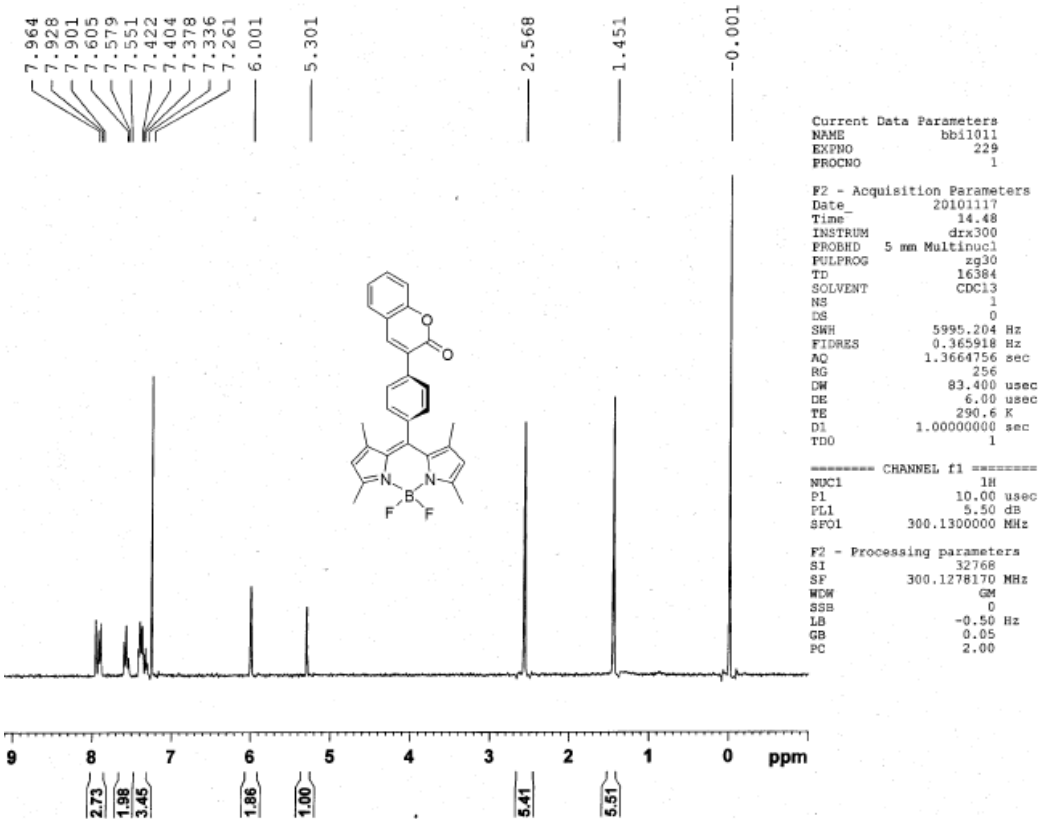

Fig. S2 ^{1}H NMR chart of **5** ($CDCl_3$, 300MHz).

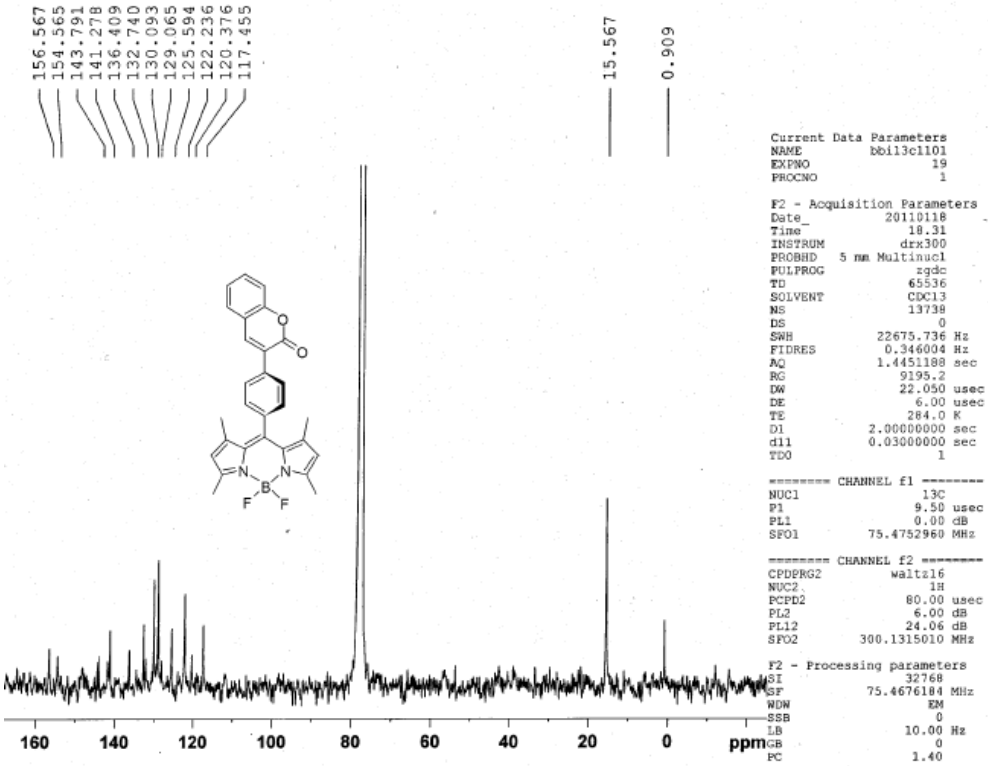

Fig. S3 ^{13}C NMR chart of **5** ($CDCl_3$, 75MHz).

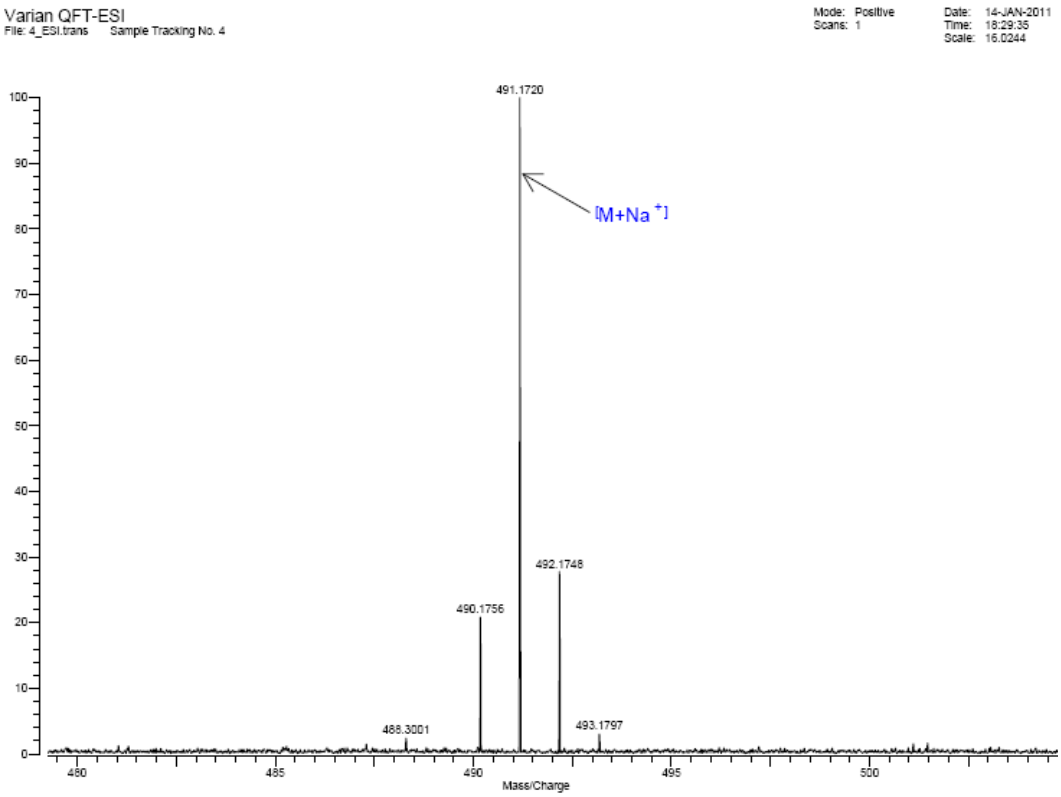

Fig. S4 HRMS chart of **5**.

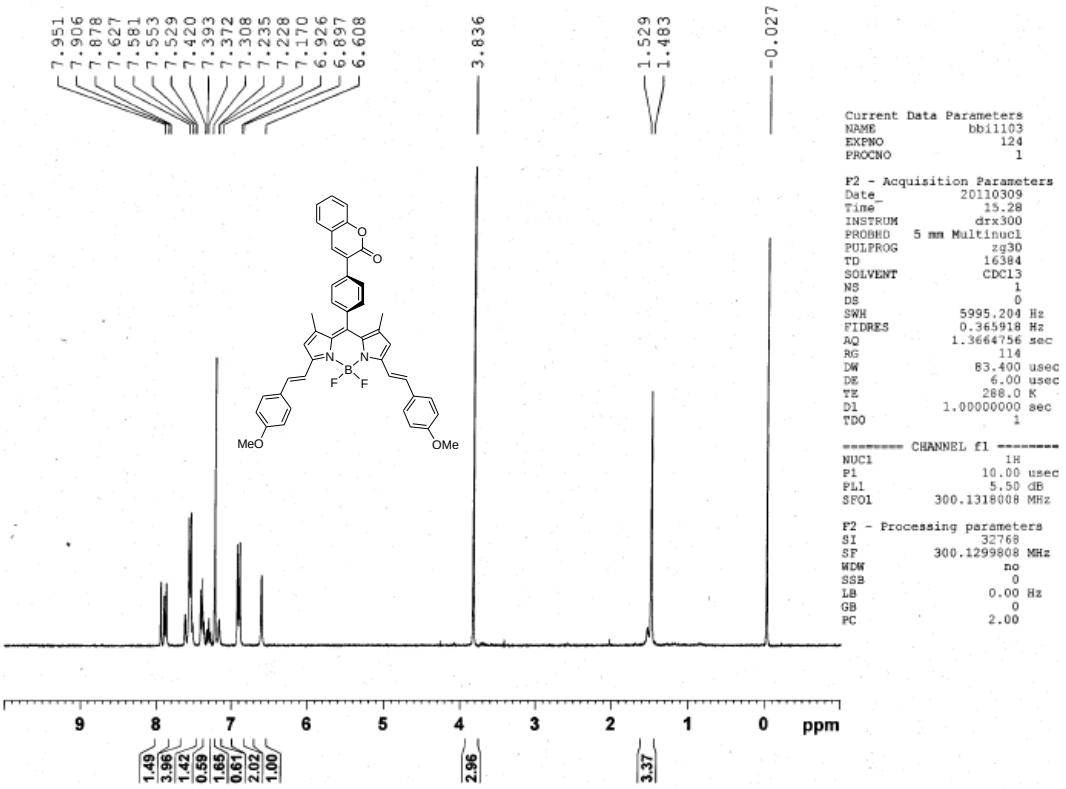

Fig. S5 ^{1}H NMR chart of **6** ($CDCl_3$, 300MHz).

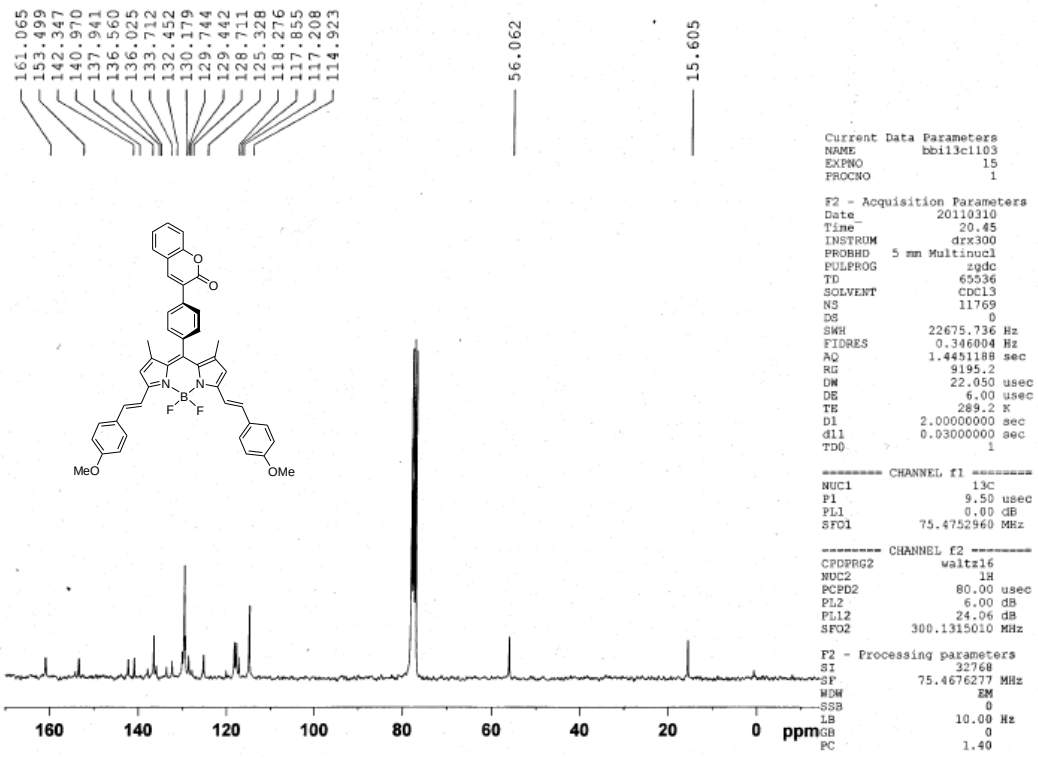

Fig. S6 ^{13}C NMR chart of **6** ($CDCl_3$, 75MHz).

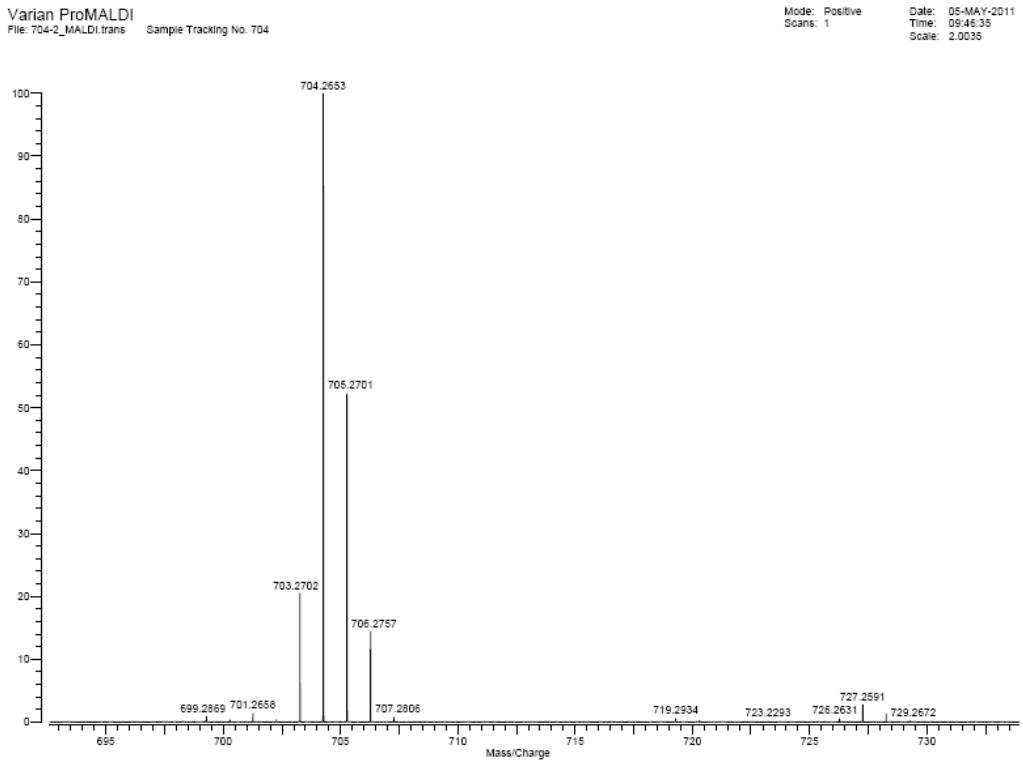

Fig. S7 HRMS chart of **6**.

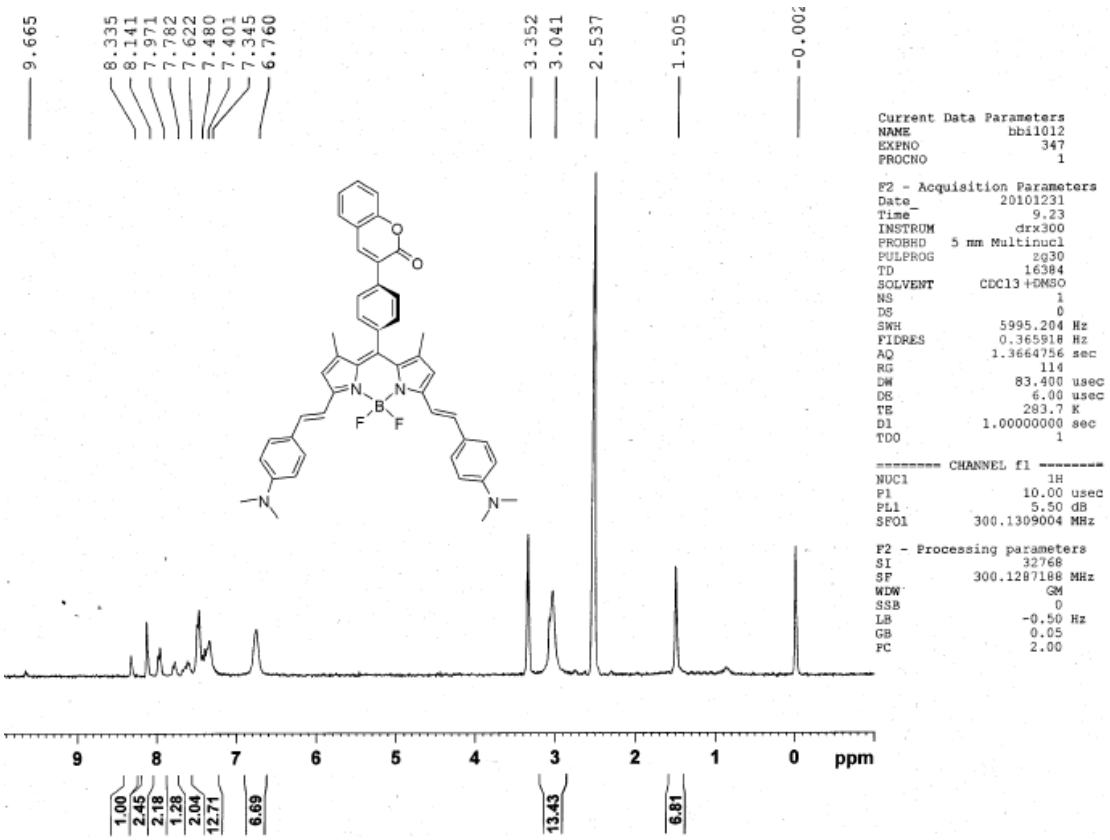

Fig. S8 ^{1}H NMR chart of **7** ($CDCl_3$/DMSO-d_6, 300MHz).

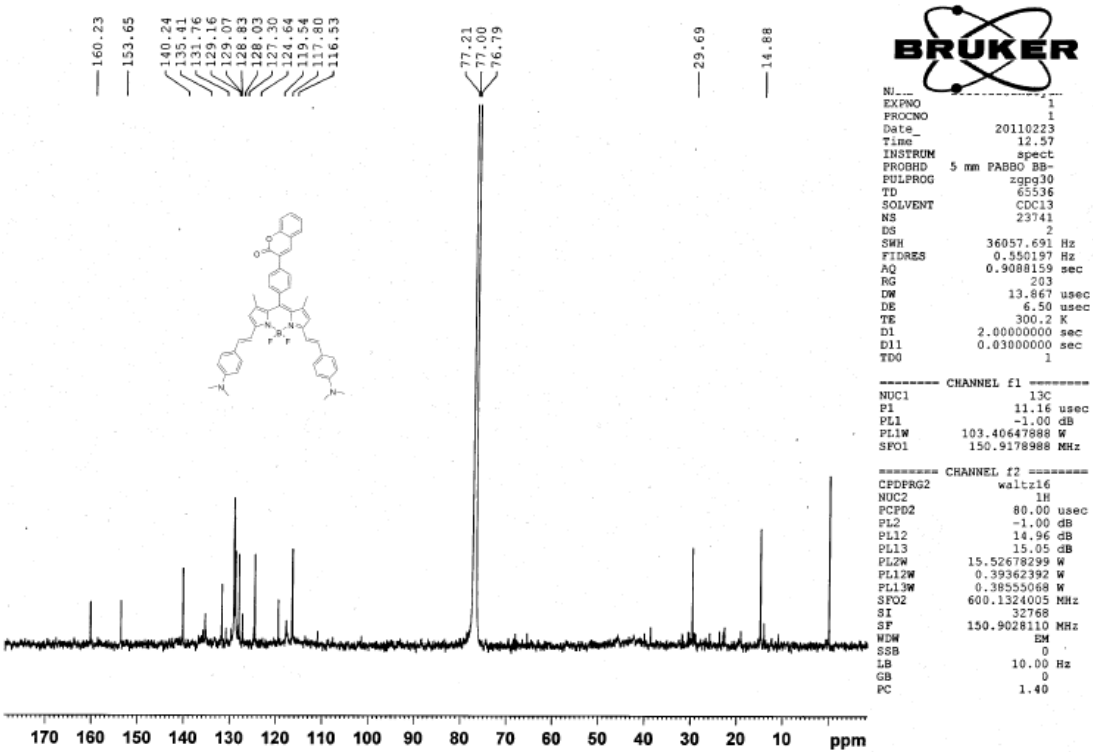

Fig. S9 ^{13}C NMR chart of **7** ($CDCl_3$, 150 MHz).

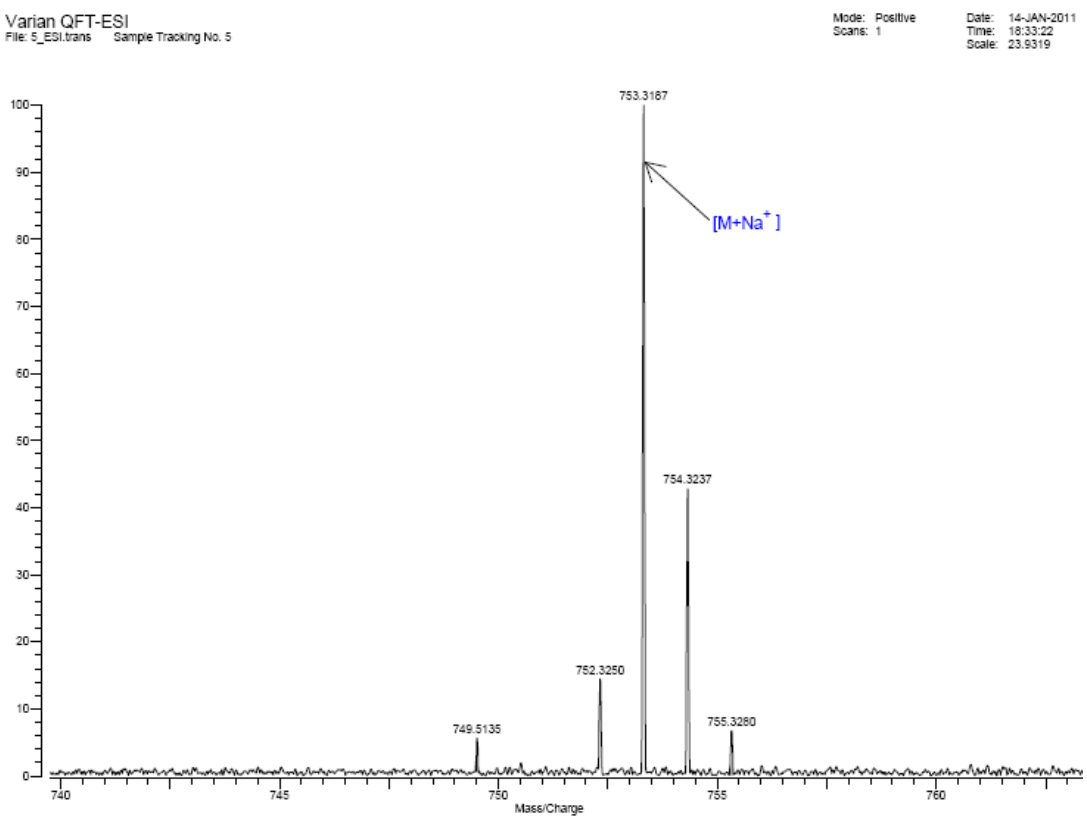

Fig. S10 HRMS chart of **7**.

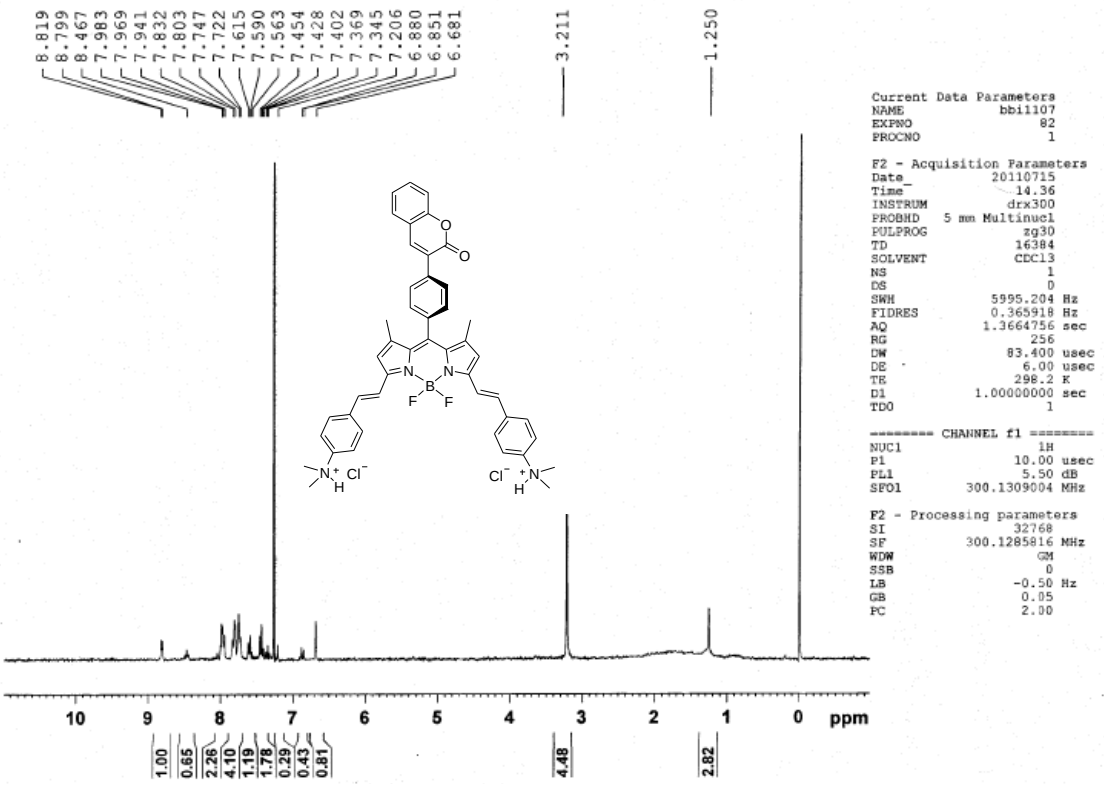

Fig. S11 ^{1}H NMR chart of **8** ($CDCl_3$, 300MHz).

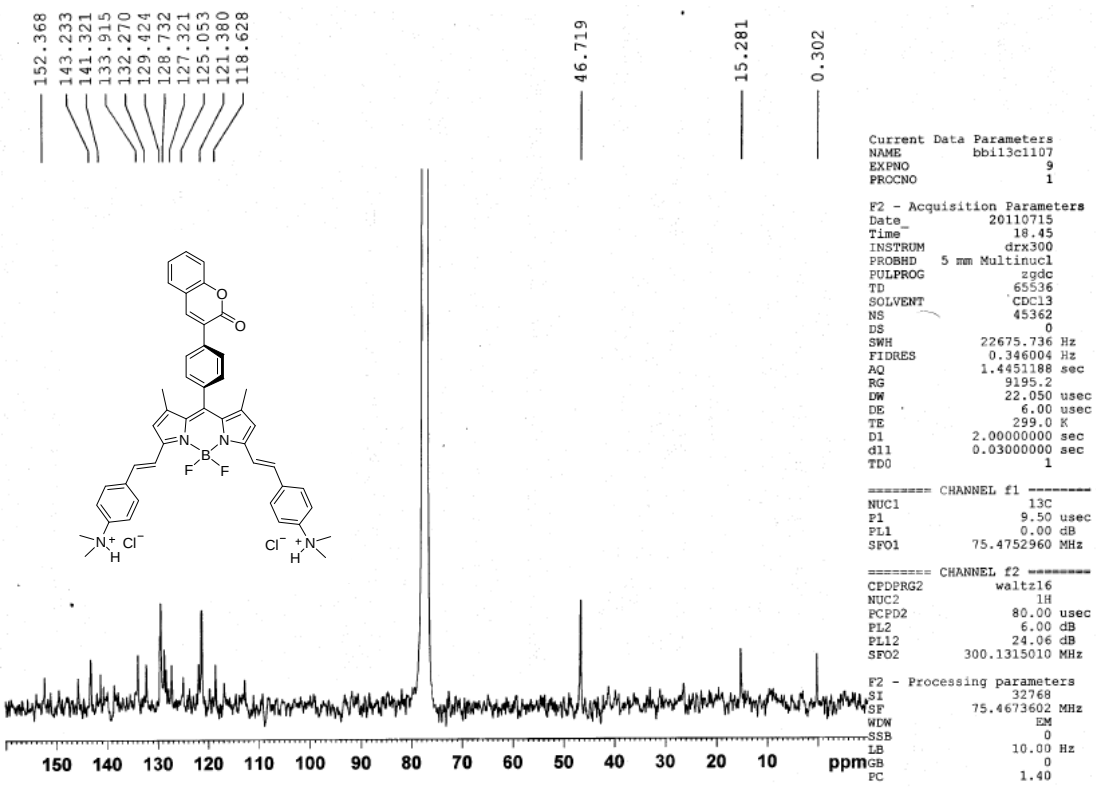

Fig. S12 ^{13}C NMR chart of **8** ($CDCl_3$, 75 MHz).

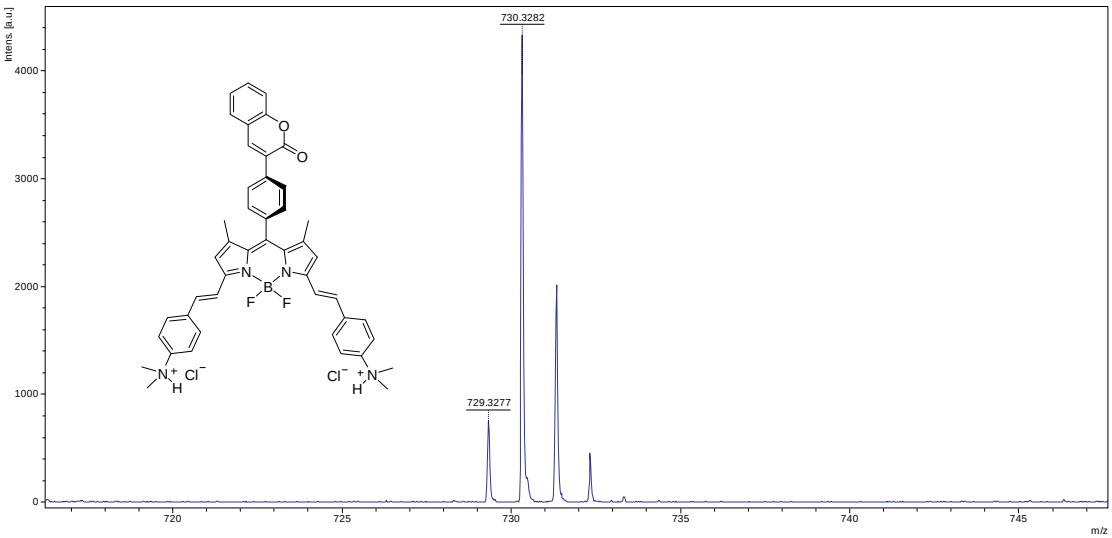

Fig. S13 HRMS chart of **8**.