

Supporting Information

Triphenylamine-cored Tetramethyl-BODIPY dyes: Synthesis, Photophysics and Lasing Properties in Organic Media

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1. Experimental Section

1.1 General

Solvents were dried and distilled according to standard procedures prior to use. All other compounds were commercially available and used as received. ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance 300 spectrometer using the solvent residue signal as the internal standard. IR spectra were recorded in diffuse reflection with a Magna 560 FT-IR spectrophotometer. All the photoluminescence (PL) spectra were measured with a Hitachi F-4500 fluorescence spectrophotometer. The UV-visible absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. The narrow-line width laser emission and tuning ranges of dye solutions were collected using an Ocean Optics Maya2000 Pro Fiber Optic Spectrometer. ASE investigations were performed using a Nd:YAG laser with a repetition rate of 10 Hz and pulse duration of about 10 ns. The laser power was detected by Newport 2936C laser power meter.

1.2 Laser experiments

Liquid solutions of dyes were contained in 1 cm optical-path quartz cells that were carefully sealed to avoid solvent evaporation during experiments. ASE investigation was performed using Q-switched pulsed Nd:YAG laser with a repetition rate of 1 Hz and pulse duration of about 10 nanosecond. The excitation 355 nm laser source was normally focused onto the quartz cells (the focused pumping stripe along the alignment of the quartz cell) in a 6 mm×0.6 mm stripe by a cylindrical lens. The polarization direction of pumping source was perpendicular to the focused pumping

stripe. The ASE radiation is generated and radiated equally in two opposite directions along the sample cells; ASE output power from one end of the sample was measured as a function of the 355 nm pump power.

1.3 Procedure for the Determination of Quantum yield

Quantum yields of the TPA-Malonitrile fluorophores were determined according to the following method: Fluorescein ($\Phi_{ST} = 0.95$) was chosen as the standard dye. Diluted solutions of the standard dye in 0.1 M NaOH, and the dye to be evaluated in the various solvents were prepared at five different concentrations. The concentrations were selected, so that the absorbance of each sample was below 0.10 at the excitation wavelength and above to prevent re-absorption. Next, a graph of the absorbance (A) at a certain wavelength (496 nm) versus the integrated emission intensity (F) excited at the chosen wavelength was plotted. Then, the slope (Grad) of the fitting line to the plot of F versus A was calculated (intercept = 0). Absolute values are calculated using the standard samples which have a fixed and known fluorescence quantum yield value, according to the following equation:

$$\Phi_X = \Phi_{ST} \left(\frac{\text{Grad}_X}{\text{Grad}_{ST}} \right) \left(\frac{n_X^2}{n_{ST}^2} \right)$$

Where the subscripts ST and X denote standard and test respectively, Φ is the fluorescence quantum yield, *Grad* the gradient from the plot of integrated fluorescence intensity vs absorbance, and *n* the refractive index of the solvent.

1.4. Synthesis of All the Intermediates

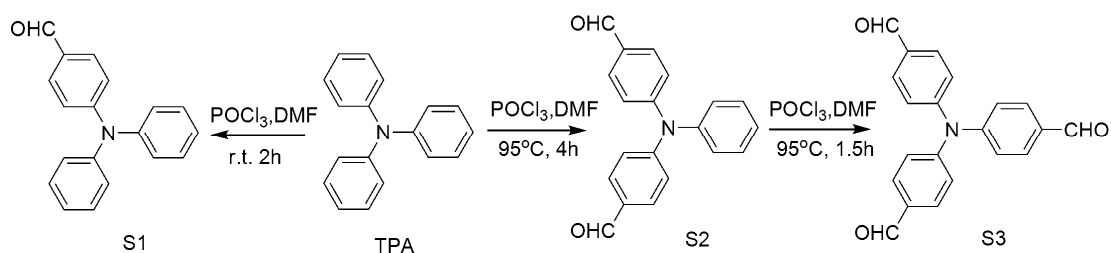
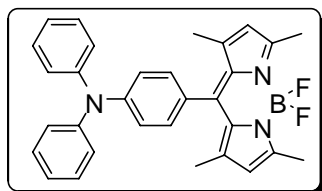
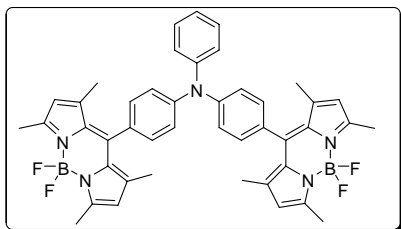


Fig. S1. Reported Synthesis of Substituted triphenylamines S1-3.



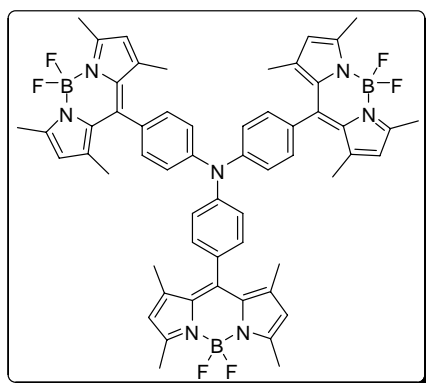
Compound 1, TPA-BDP1: This compound was synthesized following the procedure reported earlier.¹

¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, J = 7.6 Hz, 5H), 7.22 – 7.01 (m, 11H), 6.01 (s, 2H), 2.56 (s, 6H), 1.59 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 155.36, 148.68, 147.54, 129.68, 129.07, 128.38, 124.94, 123.59, 121.37, 14.85; IR (KBr, cm⁻¹): ν = 2913, 2675, 2360, 1590, 1543, 1496, 1375, 1307, 1152, 1075, 972, 808, 693, 472.



Compound 2. TPA-BDP2: A solution of 4,4'-(phenylazanediyl)dibenzaldehyde (1.0 mmol, 0.301 g), 2,4-dimethyl pyrrole (4.0 mmol, 0.38 g) and one drop of trifluoroacetic acid (TFA) in anhydrous CH₂Cl₂ (50 mL) was stirred overnight under nitrogen atmosphere at room temperature. The red solution was treated with *p*-chloranil (2.0 mmol, 0.492 g), stirring was continued for 30 min followed by the addition of Et₃N (3 mL) and BF₃·Et₂O (4 mL) under ice-cold conditions. The mixture was stirred at room temperature for further 3 h. The reaction mixture was washed with

water (3×100 mL), and the organic layers were combined and dried over anhydrous MgSO₄. The solvent was concentrated at reduced pressure, and the residue was purified by column chromatography (silica gel, petroleum ether: EtOAc = 10:1, v/v) to give the compound **2** as a red powder in 25% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.37 – 7.30 (m, 3H), 7.16 (dd, J = 16.5, 7.8 Hz, 10H), 6.01 (s, 4H), 2.56 (s, 12H), 1.59 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 155.49, 148.11, 142.82, 131.70, 129.77, 129.29, 125.30, 124.30, 123.93, 121.27, 14.53; IR (KBr, cm⁻¹): ν = 2937, 2739, 2677, 2491, 1596, 1544, 1471, 1401, 1308, 1155, 1037, 981, 804, 696, 527, 474. EI-MS: *m/z* = 738.3. Anal. Calcd for C₄₄H₄₁B₂F₄N₅: C, 71.66; H, 5.60; N, 9.50. Found: C, 71.43; H, 5.48; N, 9.25.



Compound 3. TPA-BDP3: 4,4',4''-nitriлотribenzaldehyde (1.0 mmol, 0.329 g), 2,4-dimethyl pyrrole (6.0 mmol, 0.57 g), *p*-chloranil (3.0 mmol, 0.738 g), Et₃N (6 mL) and BF₃·Et₂O (8 mL) were used in accordance with the general procedure given above. The product **3** was obtained as a red powder in 20% yield. ¹H NMR (300 MHz, CDCl₃) δ 7.23 (s, 12H), 6.02 (s, 6H), 2.56 (s, 18H), 1.59 (s, 18H); ¹³C NMR (75 MHz, CDCl₃) δ 155.70, 147.64, 143.79, 141.04, 131.58, 142.67, 130.16, 129.64, 124.50, 121.38, 14.55; IR (KBr, cm⁻¹): ν = 2920, 2852, 1600, 1545, 1511, 1440, 1372, 1308,

1194, 1154, 1077, 1050, 975, 829, 709, 475. EI-MS: $m/z = 984.5$. Anal. Calcd for $C_{57}H_{54}B_3F_6N_7$: C, 69.61; H, 5.53; N, 9.97. Found: C, 69.32; H, 5.35; N, 9.68.

Reference:

- (a) Wijesinghe, C. A.; El-Khouly, M. E.; Subbaiyan, N. K.; Supur, M.; Zandler, M. E.; Ohkubo, K.; Fukuzumi, S.; D'Souza, F. *Chem. Eur. J.* **2011**, *17*, 3147–3156. (b) Li, W.; Xie, Z.; Jing, X. *Catal. Commun.* **2011**, *16*, 94–97.

2. Photophysics and Lasing Properties

2.1 Photophysical properties of compound 1-3

Scheme 2.1 Photophysical properties of TPA-BDP1

Solvent	$E_T(30)$	λ_{abs}/nm	λ_{em}/nm	λ_{ex}/nm	$\Delta\lambda_{st}/nm$	$\Delta\nu/cm^{-1}$
Hexane	31.0	501	512	501	11	429
CCl ₄	32.4	503.5	518.4	504	14	536
Toluene	33.9	503.5	516.6	503.8	13	501
Ether	34.5	499	509.8	499	11	432
THF	37.4	500.5	511.8,593.4	502.4	9	441
EtOAc	38.1	499	509.8,590.2	499.4	10	425
CHCl ₃	39.1	502.5	513.8,618	503.6	10	438
CH ₂ Cl ₂	40.7	501	513,616.8	501.8	11	467
Acetone	42.2	498.2	512	502	10	549
MeCN	45.6	497.5	511.2	501.2	10	539
EtOH	51.9	499	512	503	9	516
MeOH	55.4	498	512.2	502.8	9	557

a. $\Delta\nu = \Delta\nu_{abs} - \Delta\nu_{em}$ b. $\Delta\lambda_{st} = \lambda_{em} - \lambda_{ex}$

Scheme 2.2 Photophysical properties of TPA-BDP2

Solvent	$E_T(30)$	λ_{abs}/nm	λ_{em}/nm	λ_{ex}/nm	$\Delta\lambda_{st}/nm$	$\Delta\nu/cm^{-1}$
Hexane	31.0	501	515.4	506	9	557
CCl ₄	32.4	504	518.6	507	11	559
Toluene	33.9	504	519.6	508.2	11	595
Ether	34.5	499.5	512.0	499.6	12	489
THF	37.4	500.5	516.6	507.2	9	623
EtOAc	38.1	498.5	513.6	503.2	10	590
CHCl ₃	39.1	503	517.2,595.4	507.2	10	546
CH ₂ Cl ₂	40.7	501	515.8,592	505.6	10	573
Acetone	42.2	499	516,617.6	507.2	9	660
MeCN	45.6	497	511.4	502.4	9	566

EtOH	51.9	499.5	513.8	505.6	8	518
MeOH	55.4	498	513.2	503.2	10	595

a. $\Delta\nu = \Delta\nu_{\text{abs}} - \Delta\nu_{\text{em}}$ b. $\Delta\lambda_{\text{st}} = \lambda_{\text{em}} - \lambda_{\text{ex}}$

Scheme 2.3 Photophysical properties of TPA-BDP3

Solvent	$E_T(30)$	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\lambda_{\text{ex}}/\text{nm}$	$\Delta\lambda_{\text{st}}/\text{nm}$	$\Delta\nu/\text{cm}^{-1}$
Hexane	31.0	501.5	515.6	504.8	11	545
CCl ₄	32.4	504.5	520.8	508	12	620
Toluene	33.9	504	519.2	508.4	11	581
Ether	34.5	499.5	512.6	500.4	12	512
THF	37.4	500.5	515.8	504.2	11	593
EtOAc	38.1	498.5	513.4	501.2	12	582
CHCl ₃	39.1	503	517.4	506.6	11	553
CH ₂ Cl ₂	40.7	501.5	516.6	505	11	583
Acetone	42.2	498.4	515, 607	505	10	646
MeCN	45.6	497.5	513	502.2	11	607
EtOH	51.9	499.5	514.2	503	11	572
MeOH	55.4	498.5	513.2	503.8	10	575

a. $\Delta\nu = \Delta\nu_{\text{abs}} - \Delta\nu_{\text{em}}$ b. $\Delta\lambda_{\text{st}} = \lambda_{\text{em}} - \lambda_{\text{ex}}$

2.2. Solvent effect on absorption spectra

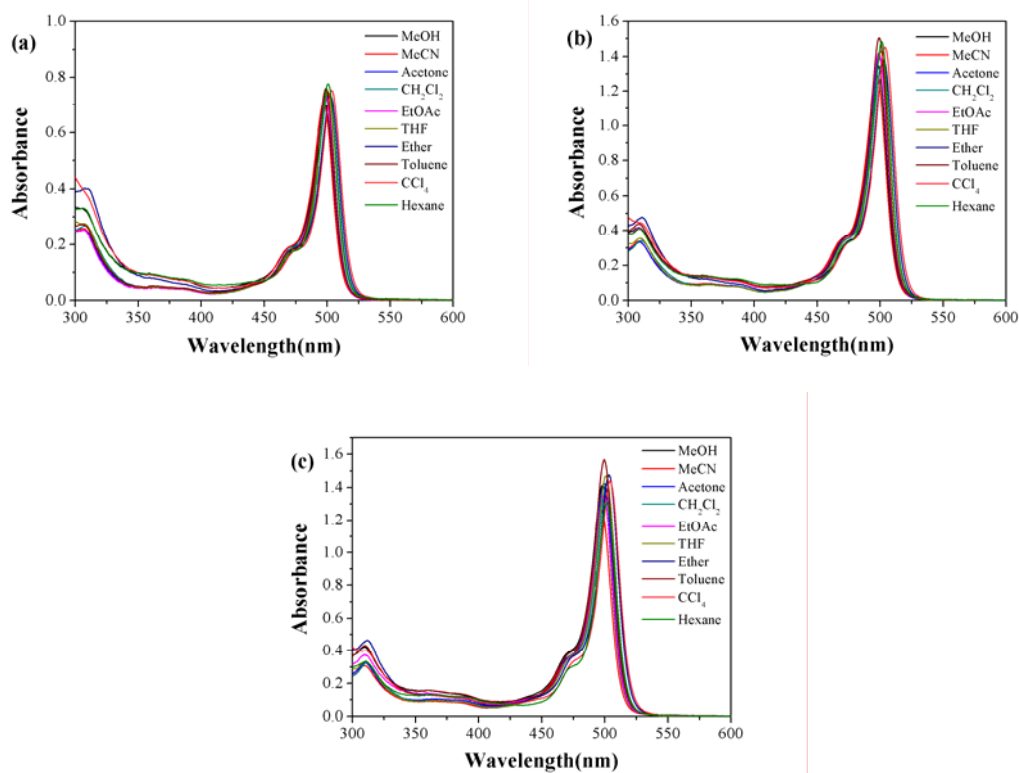


Fig. S2. Overlapped absorbance spectra of (a) TPA-BDP1, (b) TPA-BDP2 and (c) TPA-BDP3 (10 μM) in different solvents.

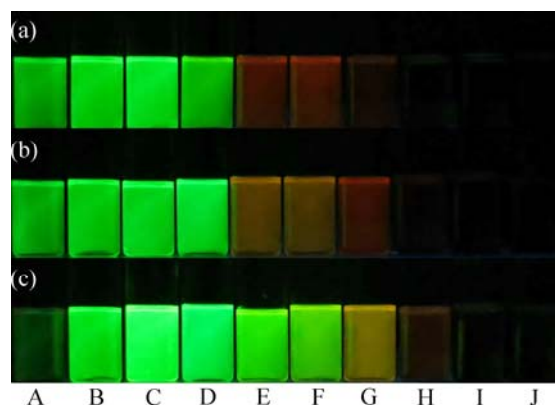
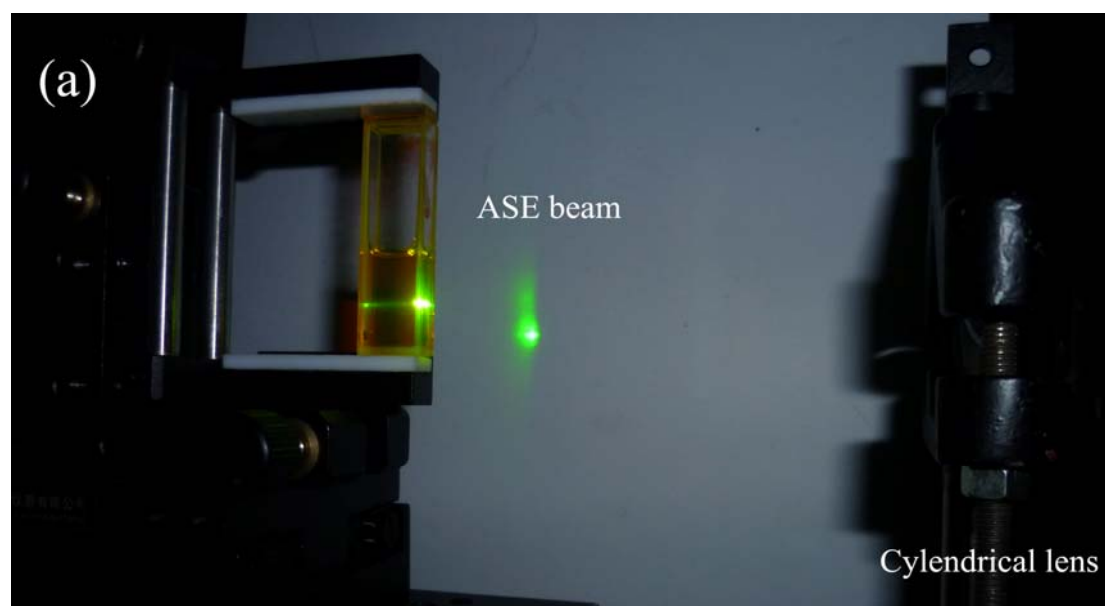


Fig. S3. Photographs of (a) TPA-BDP1, (b) TPA-BDP2 and (c) TPA-BDP3 taken under UV illumination in different solvents: (A) hexane, (B) CCl₄, (C) toluene, (D) ethyl ether, (E) THF, (F) ethyl acetate, (G) dichloromethane, (H) acetone, (I) acetonitrile, and (J) methanol.

2.3. Laser Action of compound 1-3 in toluene

Table S4. Laser parameters of TPA-BDP1-3 in different solvents pump at 355nm

Dye	Data	Hexane	CCl ₄	Toluene	Ether	THF	EtOAc	CHCl ₃	MeOH
TPA-BDP1	ASE efficiency (%)	2	0	9	0.62	0	0	0	0
	Slope efficiency (%)	2.17	0	5.6	0.32	0	0	0	0
	Threshold Energy (μJ)	850	0	200	900	0	0	0	0
TPA-BDP2	ASE efficiency (%)	0.64	0	7.4	0.38	0	0	0	0
	Slope efficiency (%)	0.31	0	4.74	0.21	0	0	0	0
	Threshold Energy (μJ)	1050	0	325	1650	0	0	0	0
TPA-BDP3	ASE efficiency (%)	0	0	7	0.26	0	0	0	0
	Slope efficiency (%)	0	0	4.2	0.1	0	0	0	0
	Threshold Energy (μJ)	0	0	400	2150	0	0	0	0



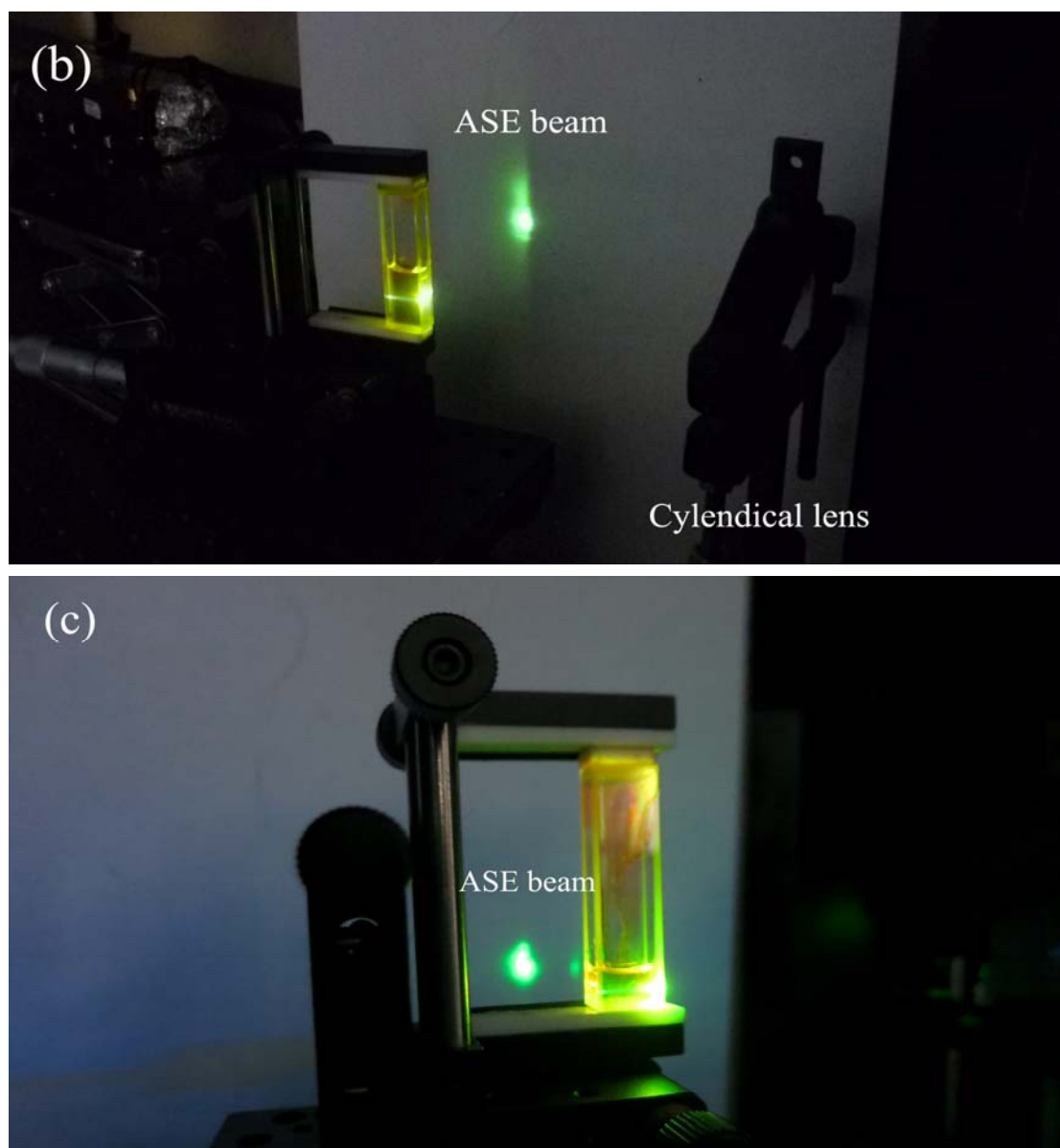


Fig. S4. Photograph of the ASE from (a) TPA-BDP1, (b) TPA-BDP2 and (c) TPA-BDP3 in toluene solution.

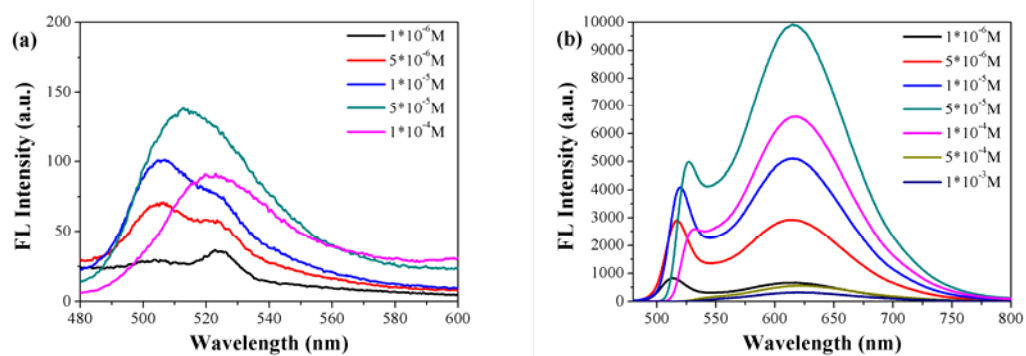
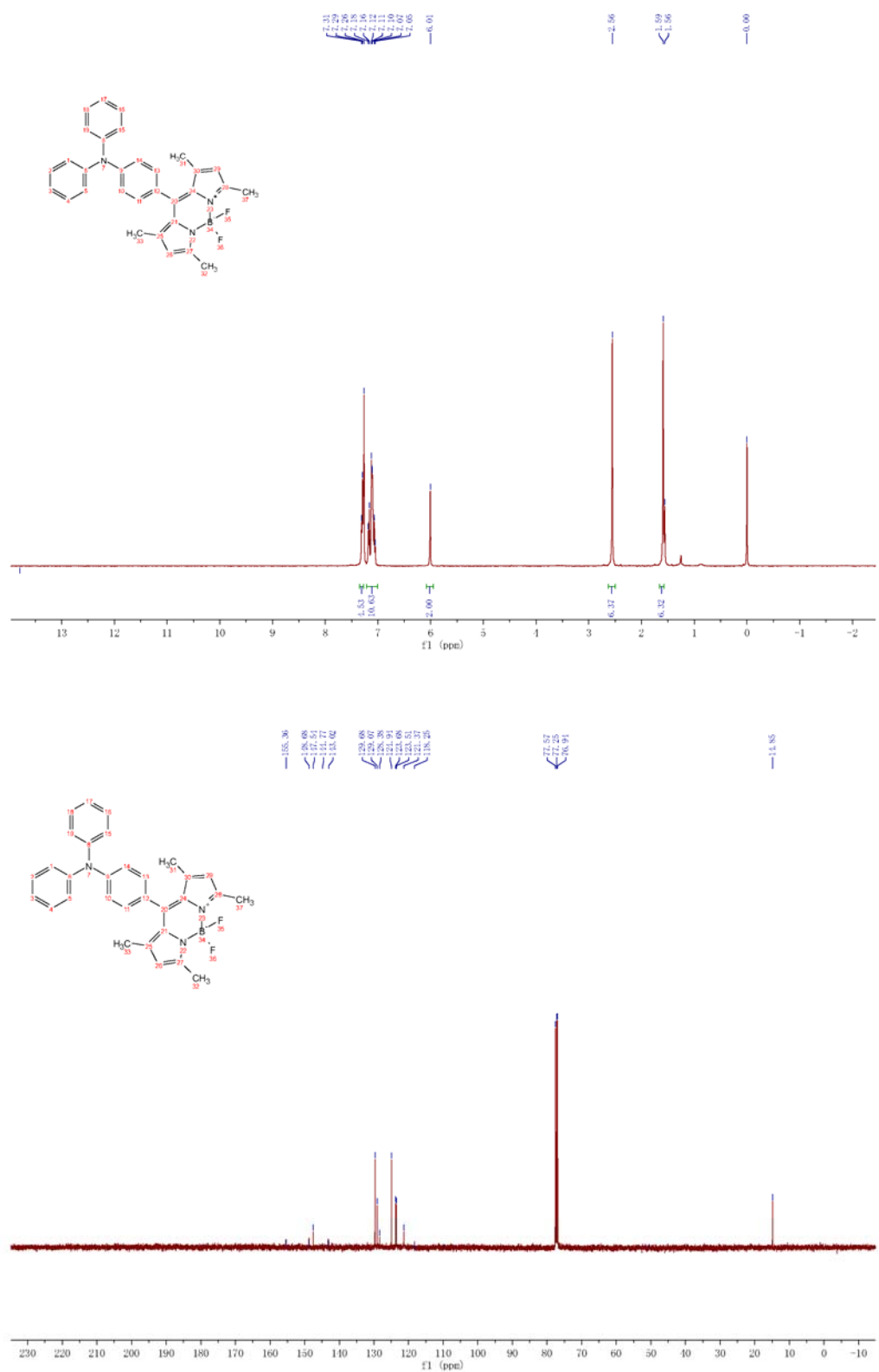


Fig. S5. A concentration dependent study of (a) TPA-BDP1, (b) TPA-BDP2 in CH_2Cl_2 taken under the F-7000 FL Spectrophotometer with slit 10.0/5.0 nm.

3. NMR and MS spectra copies

3.1. ^1H and ^{13}C NMR of compound 1-3



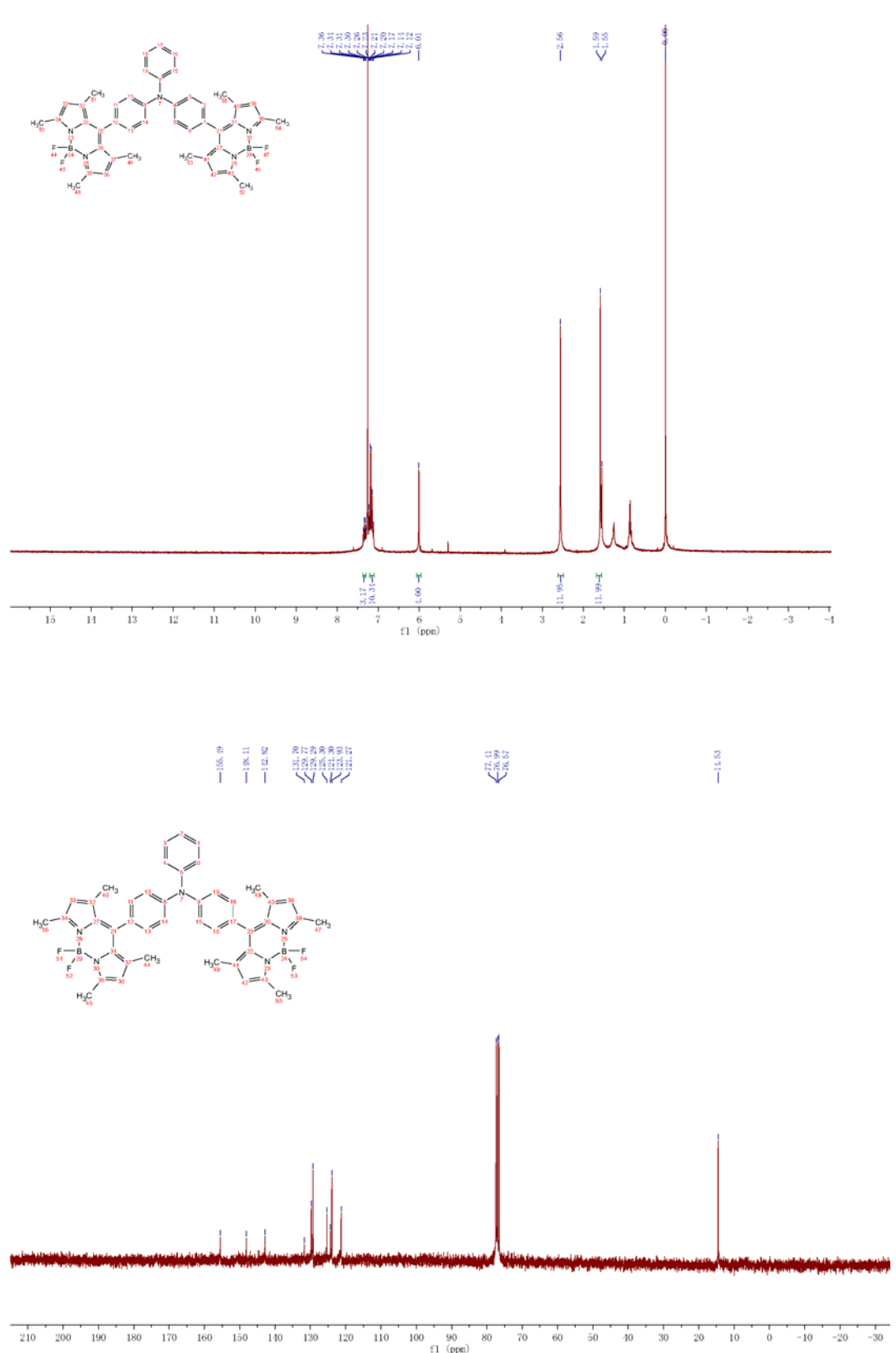


Fig. S7. The ^1H and ^{13}C NMR spectra of compound **TPA-BDP2** in CDCl_3 .

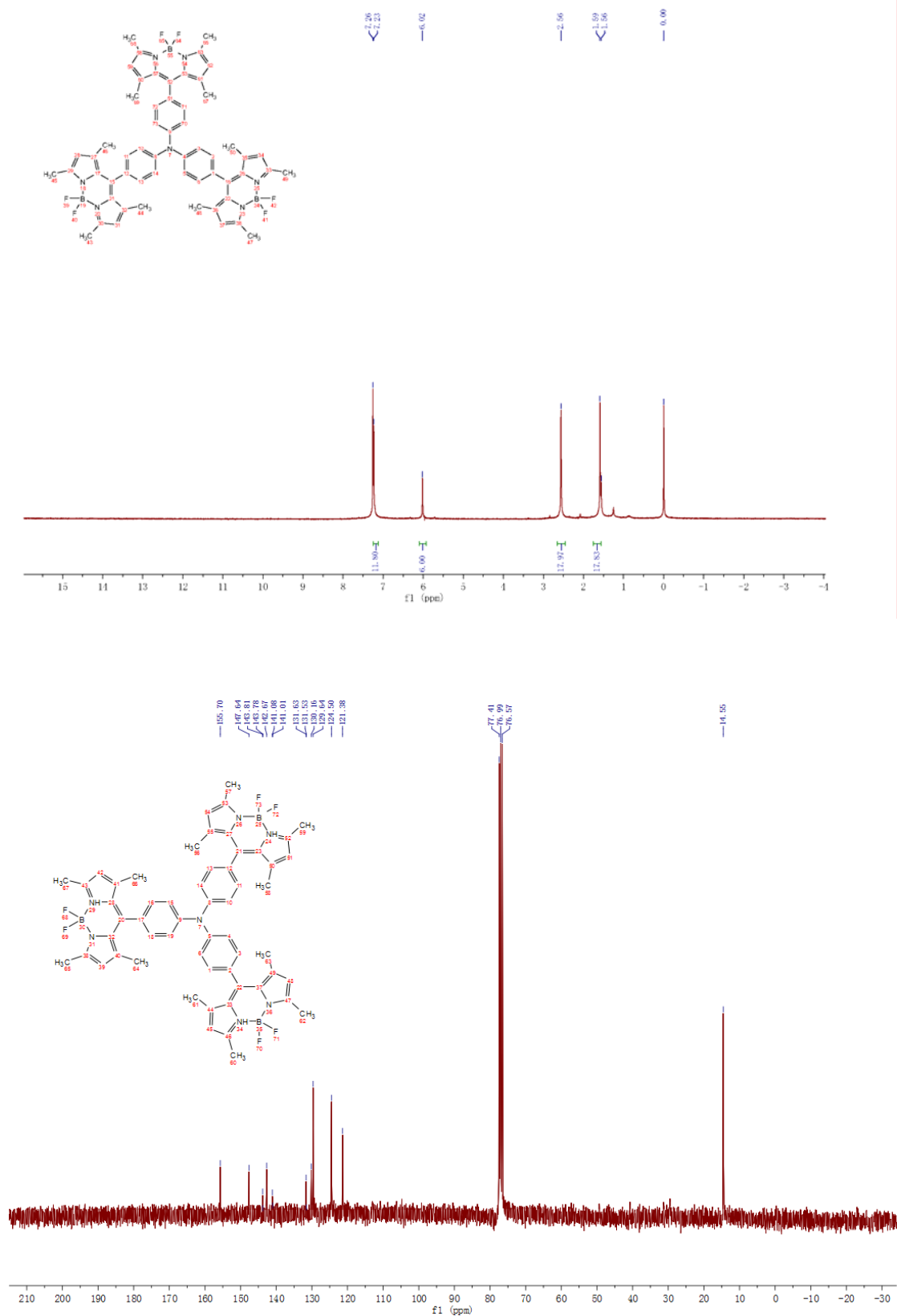


Fig. S8. The ^1H and ^{13}C NMR spectra of compound **TPA-BDP3** in CDCl_3 .

3.2. ESI-MS spectra of compound TPA-BDP2 and 3

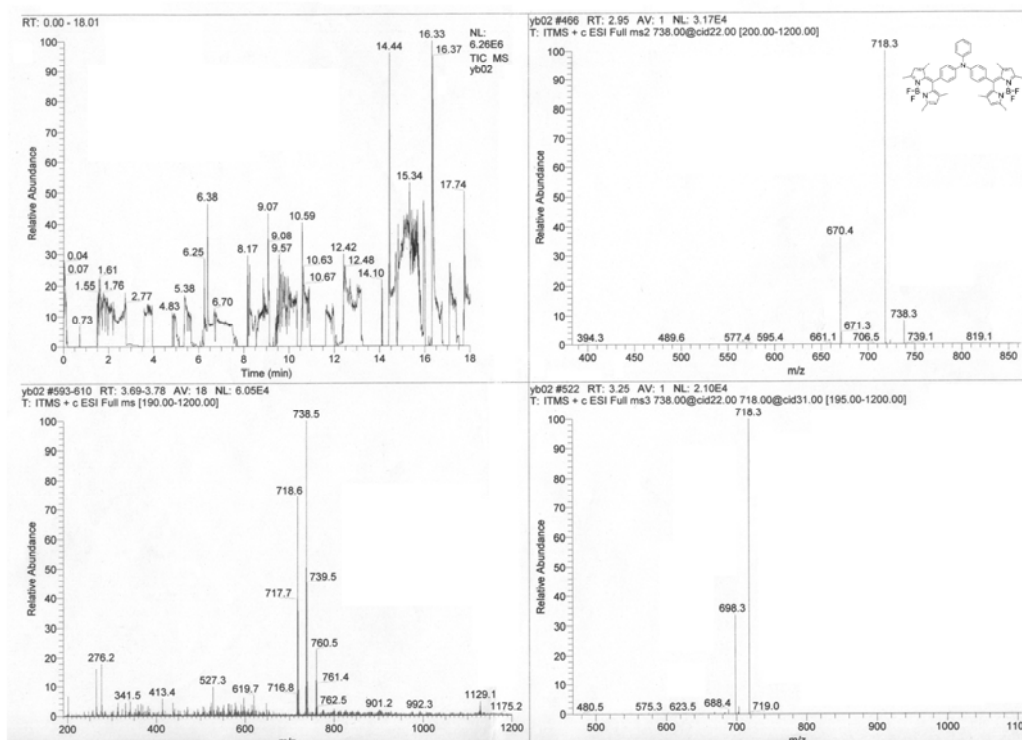


Fig. S9. The ESI-MS spectra of compound TPA-BDP2

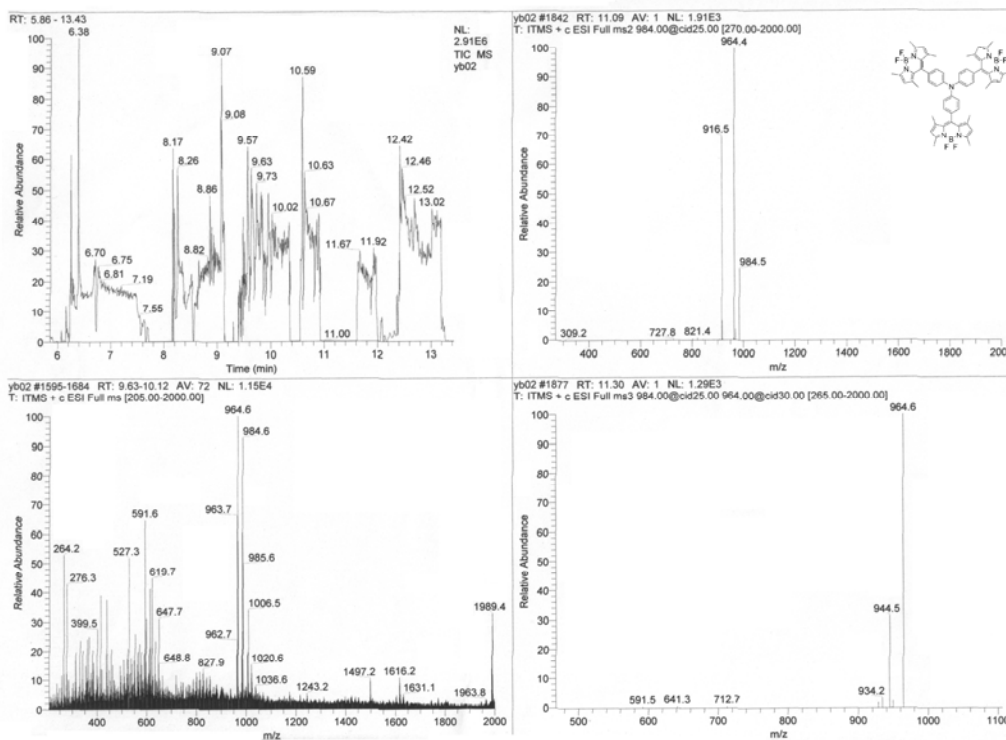


Fig. S10. The ESI-MS spectra of compound TPA-BDP3