Electronic Supplementary Information

Multibranched triarylamine end-capped triazine derivatives with aggregation-induced emission properties and large two-photon absorption cross-sections

Yihua Jiang,[a] Yaochan Wang,[b] Jianli Hua,*[a] Jin Tang,[a] Bo Li,[c] Shixiong Qian,[b] and He Tian*[a]

[a]Key Laboratory for Advanced Materials and Institute of Fine Chemicals,

East China University of Science & Technology, Shanghai 200237 (P.R. China)

[b]Department of Physics, Fudan University, Shanghai 200433 (P.R. China)

[c]Key Laboratory of Polar Materials and Devices, Ministry of Education, East China Normal University, 500 Dongchuan Road, Shanghai 200241(P.R. China)

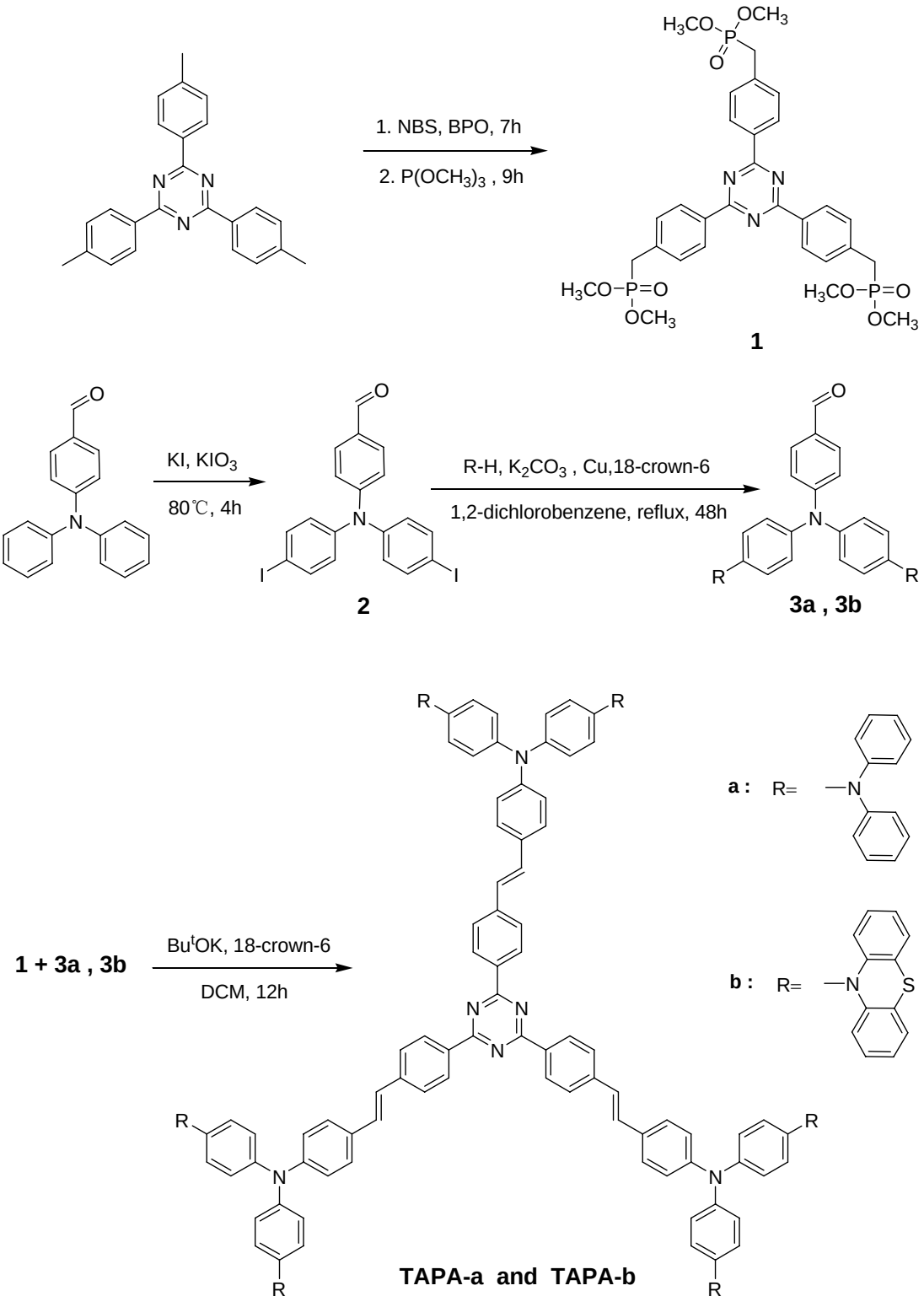
E-mail: jlhua@ecust.edu.cn; tianhe@ecust.edu.cn. fax: +86-21-64252758.

Materials Synthesis

Tetrahydrofuran (THF) was pre-dried over 4 Å molecular sieves and distilled under argon atmosphere from sodium benzophenone ketyl immediately prior to use. Triethylamine was distillated under normal pressure and dried over potassium hydroxide. *N, N*-dimethyl formamide (DMF) and dichloromethane (DCM) were reflux with calcium hydride and distilled before used. Starting materials 2,4,6-Tri (p-tolyl)-1,3,5-triazine, 4-(diphenylamine)benzaldehyde were prepared according to published procedures.[1] All other chemicals were purchased from Aldrich and used as received without further purification.

Instruments

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer using chloroform-*d* as solvent and tetramethylsilane ($\delta = 0$) as internal references. The UV/Vis spectra were recorded on a Varian-Cary 500 spectrophotometer with 2 nm resolution at room temperature. The fluorescence spectra were taken on a Varian-Cary fluorescence spectrophotometer. SEM micrographs were obtained on a JEOL JSM-6360 scanning electron microscope. TPA cross section of TAPA-a and TAPA-b was measured by femtosecond open-aperture Z-scan technique according to previously described method.[2] Two-photon excited fluorescence (TPF) was excited by the fs pulses with different intensities at wavelength of 800 nm. The repetition rate of the laser pulses is 250 kHz and the pulse duration is 80 fs.



Scheme S1 Synthetic routes to the **TAPA**-based compounds

Synthesis

Synthetic details are shown in Scheme S1. Bromination of 2, 4, 6-tri(p-tolyl)-1, 3, 5-triazine afforded 2, 4, 6- tris(4-(bromomethyl)phenyl)-1, 3, 5-triazine, followed by reaction with trimethyl phosphate, yielding triazine derivative **1**. The important intermediate aldehydes **3a** and **3b** were synthesized by Ullmann reaction from triphenylamine aldehyde iodide (**2**). Finally, condensation of the aldehyde (**3a** and **3b**) with triazine moiety (**1**) by the Horner-Wadsworth-Emmons reaction gave the target compounds **TAPA-a** and **TAPA-b**. Their structures were characterized by spectroscopy methods.

(4,4',4''-(1,3,5-Triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(methylene)triphosphonate (1). In a 100 mL round-bottom flask, 2,4,6-Tri（p-tolyl）-1,3,5-triazine (3.51 g, 0.01 mol), NBS (5.34 g 0.03 mol) and BPO (0.3 g, 1.2 mmol) were dissolved into 50 mL chlorobenzene and heated at 110 ^{o}C for 7 h. The mixture was filtered and the solvent was removed under vacuum. The resident was dissolved into trimethyl phosphite (10 mL) and refluxed for 9 h. The excessive trimethyl phosphite was removed under vacuum. The residue was purified by column chromatography on silica (ethanol: dichloromethane = 1:10, v/v) to afford the product as a white powder (5.3 g, yield: 78 %).^{1}H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 8.71 (d, 6H, *J* = 8.0 Hz), 7.51 (m, 6H), 3.61 (d, 18H, *J* = 10.8 Hz), 3.30 (d, 6H, *J* = 22.0 Hz).. ^{13}C NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): δ = 171.3, 136.3, 136.2, 135.0, 135.0, 130.1, 130.1, 129.3, 129.2, 53.1, 53.0, 33.9, 32.5. HRMS (EI) (m/z): [M] Calcd for $C_{30}H_{36}N_3O_9P_3$: 675.1664, Found: 675.1663

4-[*N*,*N*-Bis(4-iodophenyl)amino]benzaldehyde (2). A modified version of a previously reported method[3] was used. In a 500 mL three-necked round-bottom flask, 4-(*N,N*-diphenylamino)benzaldehyde (14.00 g, 51.28 mmol), potassium iodide (11.43 g, 68.85 mmol), acetic acid (210 mL) and water (20 mL) were heated to 80 ^{o}C. After stirring for 1 h, potassium iodate (10.97 g, 51.26 mmol) was added and the reaction was stirred at 80 ^{o}C for 4 h. The solution was allowed to cool and the solid was collected, washed with

water and recrystallised from DCM–ethanol (1: 5) giving the product as a yellow powder (20.05 g, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 9.89 (s, 1H), 7.75 (d, 2H, *J* = 9.0 Hz), 7.67 (d, 4H, *J* = 9.0 Hz), 7.09 (d, 2H, *J* = 9.0 Hz), 6.93 (d, 4H, *J* = 9.0 Hz). MS(EI) (*m*/*z*): [M] Calcd for $C_{19}H_{13}I_2NO$: 524.9, Found: 525.2.

4-{*N,N*-Bis[4-(*N,N*-diphenylamino)phenyl]amino}benzaldehyde (3a). A modified version of a previously reported method[3] was used. In a 250 mL round-bottom flask, 4-[*N,N*-di(4-iodophenyl)amino]-benzaldehyde (12 g, 22.86 mmol), *N,N*-diphenylamine (11.62 g, 68.76 mmol), potassium carbonate (25.98 g, 188.26 mmol), activated copper bronze (8.80 g, 138.58 mmol) and 18-crown-6 (1.20 g, 4.55 mmol) were refluxed in 1,2-dichlorobenzene (100 mL) for 48 h under argon atmosphere. The mixture was filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica (petroleum ether: dichloromethane = 1:1, v/v) to afford the product as a yellow powder (8.3 g, yield: 60 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 9.77 (s, 1H,), 7.74 (d, 2H, *J* = 9.0 Hz), 7.35 (t, 8H, *J* = 8.0 Hz), 7.18 (d, 4H, *J* = 9.0 Hz), 7.05–7.12 (m, 12H), 7.03 (d, 4H, *J* = 9.0 Hz), 6.92 (d, 2H, *J* = 9.0 Hz). MS (EI) (*m*/*z*): [M] Calcd for $C_{43}H_{33}N_3O$: 607.3, Found: 607.2.

4-{*N,N*-Bis[4-(N-phenothiazinyl)phenyl]amino}benzaldehyde (3b). A modified version of a previously reported method[3] was used. In a 250 mL round-bottom flask, 4-[*N,N*-di(4-iodophenyl)amino]benzaldehyde (12 g, 22.86 mmol), phenothiazine (13.85 g, 69.60 mmol), potassium carbonate (25.98 g, 188.26 mmol), activated copper bronze (8.80 g, 138.58 mmol) and 18-crown-6 (1.20 g, 4.55 mmol) were refluxed in 1,2-dichlorobenzene (100 mL) for 48 h under argon atmosphere. The mixture was filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica (petroleum ether: dichloromethane = 1:1, v/v) to afford the product as a yellow powder (8.09 g, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 9.88 (s, 1H), 7.88 (d, 2H, *J* = 9.0 Hz), 7.47 (d, 8H, *J* = 4.0 Hz), 7.28 (d,

2H, *J* = 9.0 Hz), 7.14 (dd, 4H, *J* = 8.1 Hz), 7.02-7.06 (m, 4H), 6.91-6.95 (m, 4H), 6.44 (dd, 4H, *J* = 8. 1 Hz). MS (EI) (*m*/*z*): [M] Calcd for $C_{43}H_{29}N_3OS_2$: 667.2, Found: 667.2.

***N*1,*N*1',*N*1''-(4,4',4''-2,2',2''-(4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(ethene-2,1-diyl)tris(benzene-4,1-diyl))tris(*N*1-(4-(diphenylamino)phenyl)-*N*4,*N*4-diphenylbenzene-1,4-diamine) (TAPA-a).** In a 250 mL round-bottom flask were added **1** (380 mg, 0.5 mmol), **3a** (300 mg, 2.0 mmol), potassium tert-butoxide (336 mg, 3.0 mmol), 18-crown-6 (20 mg, 0.08 mmol) and 100 mL DCM under argon atmosphere. After stirring at 45 ^{o}C for 6 h, the mixture was pour into distilled water and extracted with dichloromethane and water. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether: dichloromethane = 4:1, v/v) the product as a yellow powder (382 mg, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 8.77 (d, 6H, *J* = 8.0 Hz), 7.70 (d, 6H, J = 8.0 Hz), 7.45–7.47 (m, 6H), 7.26–7.30 (m, 36H), 7.11–7.15 (m, 30H), 7.04 (m, 30H). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (TMS, ppm): δ = 171.1, 147.8, 143.3, 141.9, 135.0, 130.2, 129.3, 129.2, 127.7, 125.9, 125.6, 125.3, 124.4, 123.9, 123.1, 122.6. MALDI-TOF: [M] Calcd for $C_{153}H_{114}N_{12}$: 2120.6, Found: 2120.9

4,4',4''-2,2',2''-(4,4',4''-(1,3,5-Triazine-2,4,6-triyl)tris(benzene-4,1-diyl))tris(ethene-2,1-diyl)tris(*N*,*N*-bis(4-(10H-phenothiazin-10-yl)phenyl)aniline) (TAPA-b). In a 250 mL round-bottom flask were added **1** (228 mg, 0.3 mmol), **3b** (603 mg, 1.0 mmol), potassium tert-butoxide (224 mg, 2.0 mmol), and 18-crown-6 (20 mg, 0.08 mmol), and 100 mL DCM under argon atmosphere. After stirring at 45 ^{o}C for 6 h, the mixture was pour into distilled water and extracted with dichloromethane and water. The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica (petroleum ether : dichloromethane = 4:1, v/v) to afford 600 mg of product as a yellow powder (yield: 55 %). ^{1}H NMR ($CDCl_3$, 400 MHz), δ (TMS, ppm): 8.79 (d, 6H, *J* =

8.0 Hz), 7.72 (d, 6H, *J* = 8.4 Hz), 7.59 (d, 6H, *J* = 8.4 Hz), 7.41 (d, 12H, *J* = 8.4 Hz), 7.33 (m, 21H), 7.19 (d, 3H, *J* = 16.0 Hz), 7.06 (d, 12H, *J* = 7.6 Hz), 6.94 (d, 12H, *J* = 7.2 Hz), 6.87 (d, 12H, *J* = 7.2 Hz), 6.40 (d, 12H, *J* = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (TMS, ppm): δ = 171.1, 146.9, 146.7, 144.4, 141.5, 135.8, 132.7, 131.7, 123.9, 123.4, 128.1, 127.3, 126.9, 126.9, 126.6, 125.7, 125.6, 124.9, 122.4, 120.6, 116.2, 115.9,. MALDI-TOF: [M] Calcd for $C_{153}H_{102}N_{12}S_6$: 2300.9, Found: 2301.3.

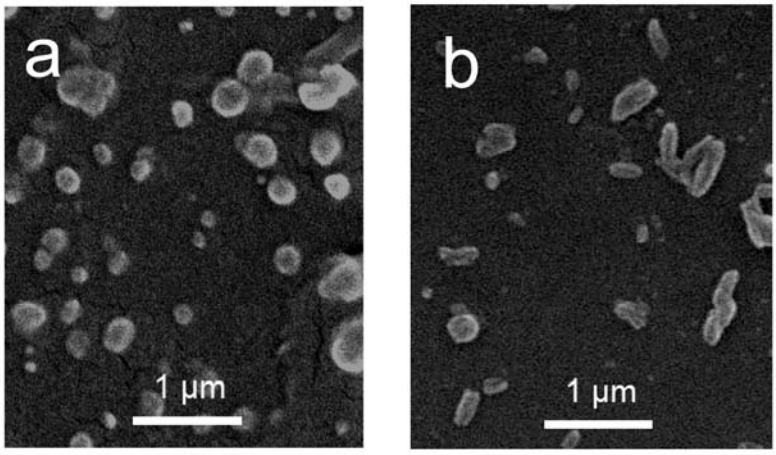


Fig. S1 SEM image of the **TAPA-a** (a) and **TAPA-b** (b) nanoaggegates prepared in THF/H_2O (= 1:9 v/v) at 1×10^{-5}M

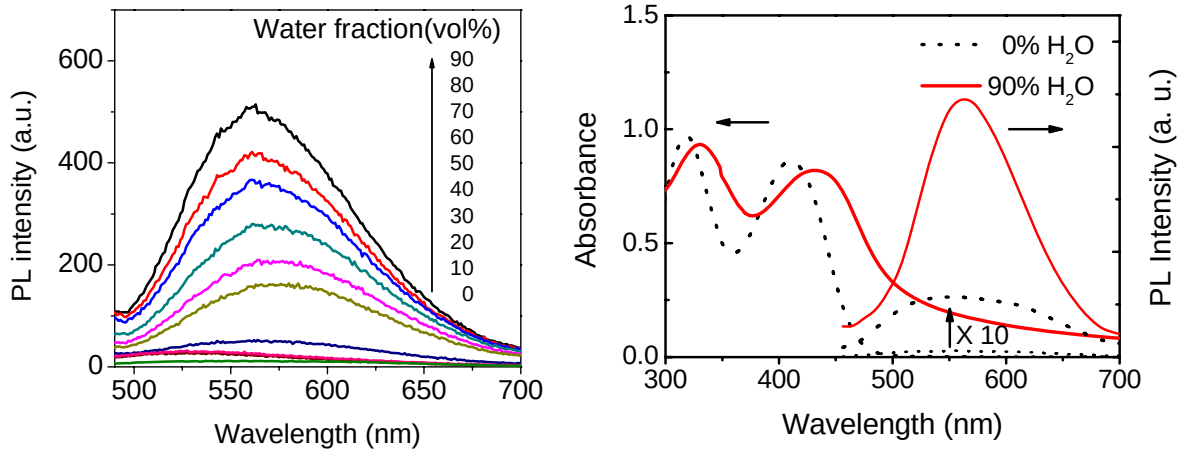


Fig. S2 Corresponding emission spectra of compound **TAPA-b** in aqueous THF with different water/THF ratios at 1×10^{-5} M.(left) Absorption and photoluminescence spectra of **TPAP-b** in solution (THF) and in dispersion of the nanoaggregate form (90% water) at 1×10^{-5} M.(right).

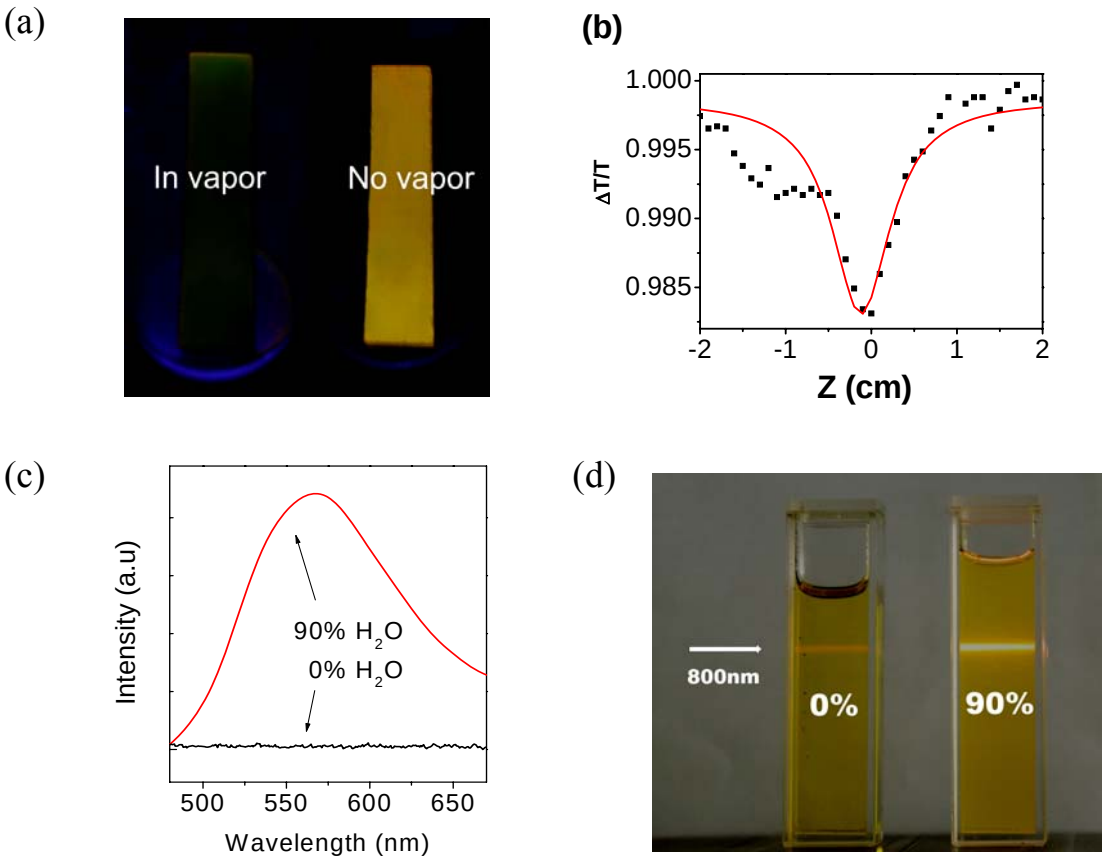


Fig. S3 (a) On/off fluorescence switching of **TAPA-b** on TLC plates in chloroform vapor (left) and without vapor (right) under UV light (365 nm) illumination at room temperature. (b) Open-Aperture Z-scan trace of **TAPA-b** (scattered circle experimental data, straight line theoretic fitted data). (c) Two-photon fluorescence emissions spectra for **TAPA-b** in solution (THF) and in dispersion of the nanoaggregate form (90% water) at 1×10^{-5} M, excited at 800 nm. (d) TPF emissions image of **TAPA-b** in the THF and water mixture (0 and 90% water).

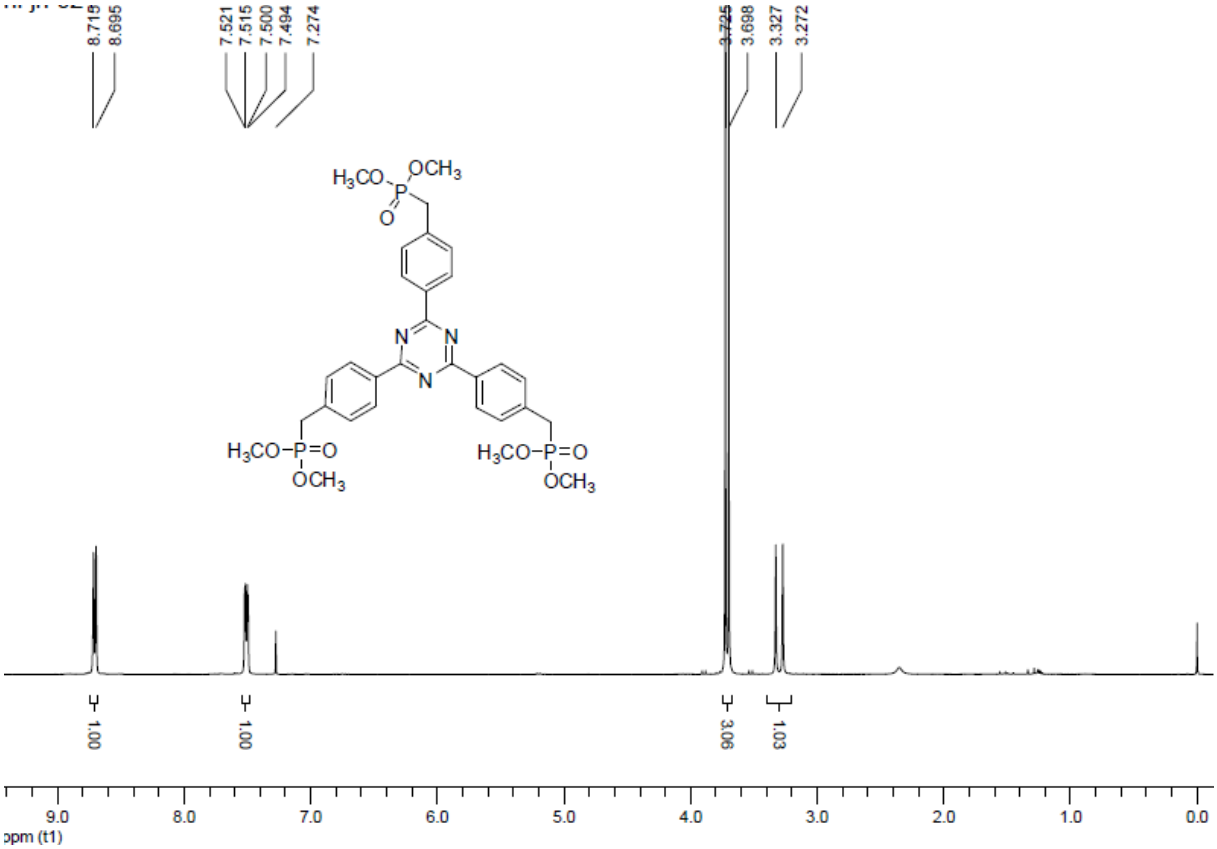


Fig. S4 ^{1}H NMR spectrum of **1** in chloroform-*d* (400MHz)

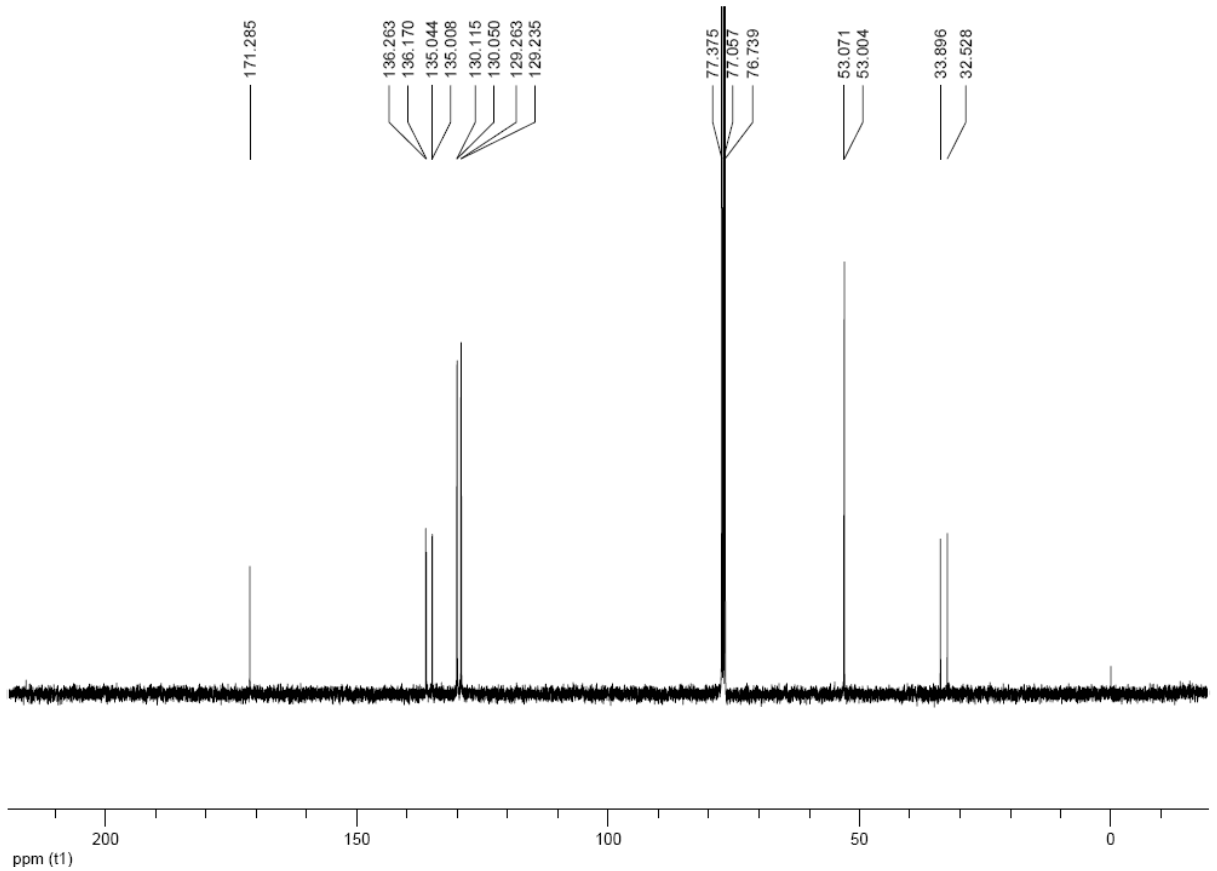


Fig. S5 ^{13}C NMR spectrum of **1** in chloroform-*d* (100MHz)

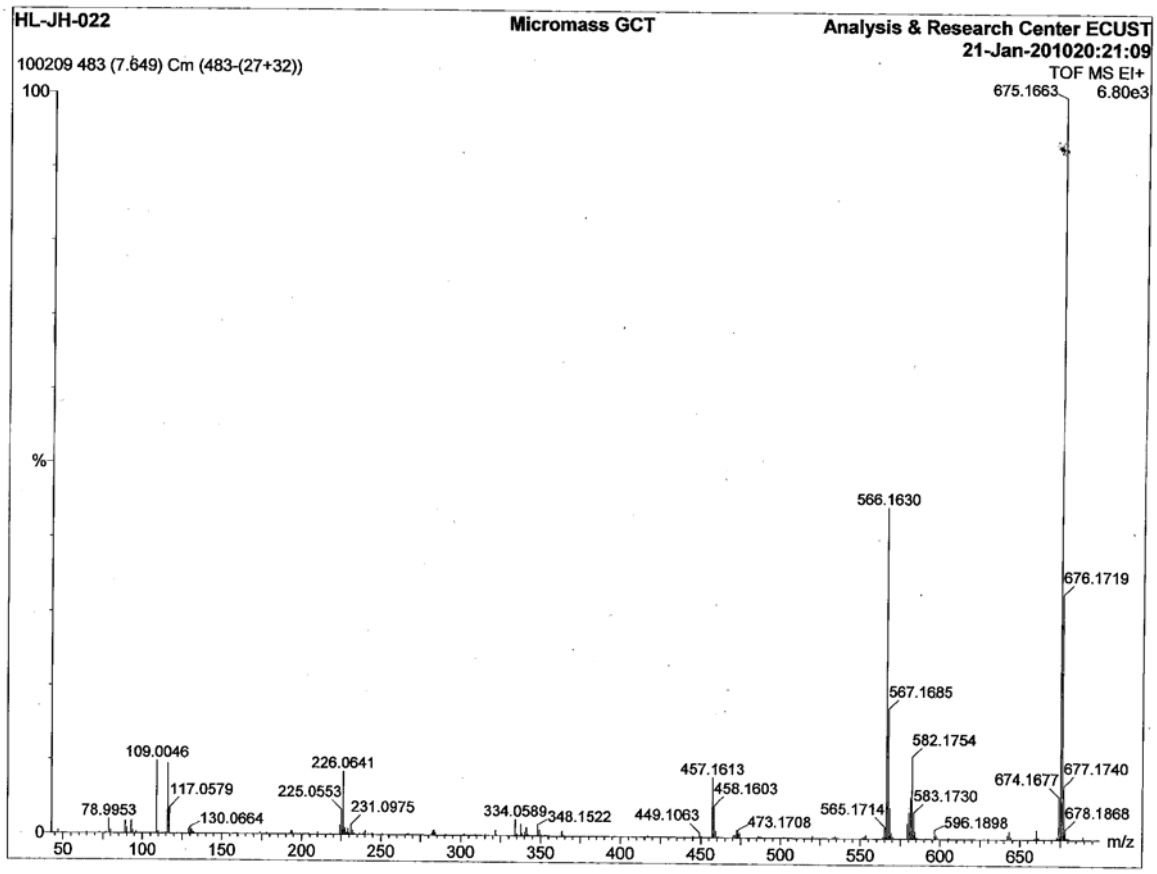


Fig. S6 MS spectrum (EI) of **1**

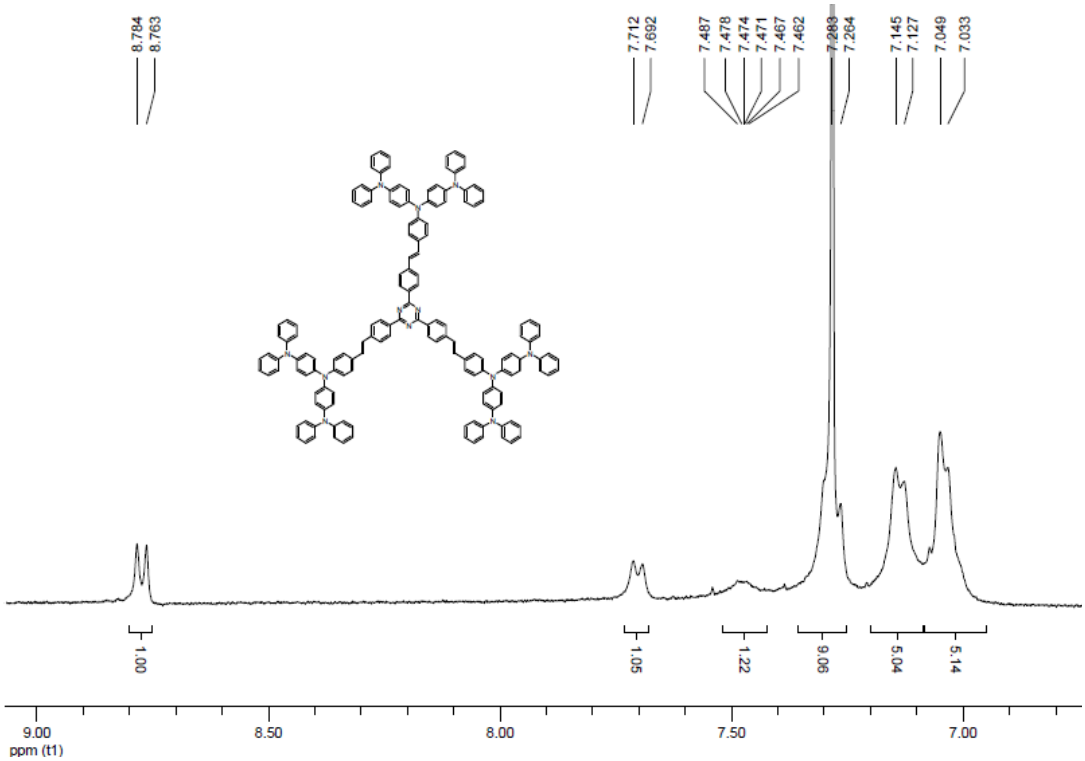


Fig. S 7 ^{1}H NMR spectrum of **TAPA-a** in chloroform-*d* (400 MHz)

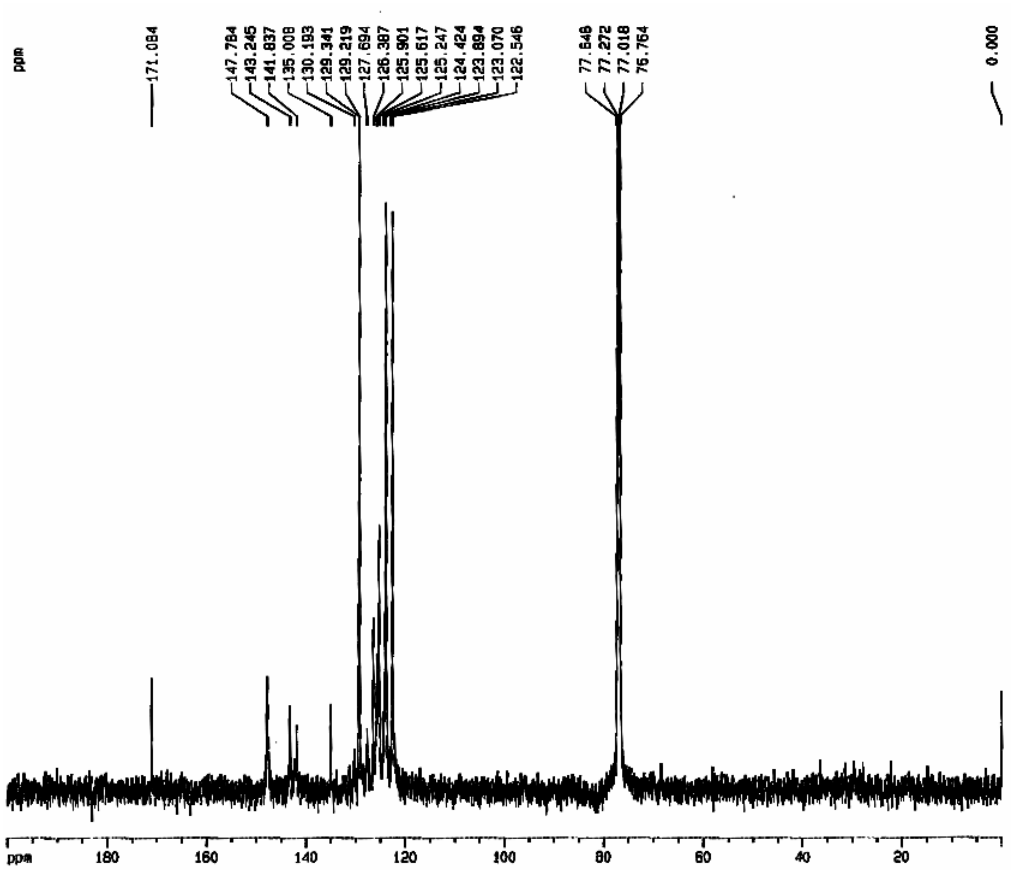


Fig. S 8 ^{13}C NMR spectrum of **TAPA-a** in chloroform-*d* (100 MHz)

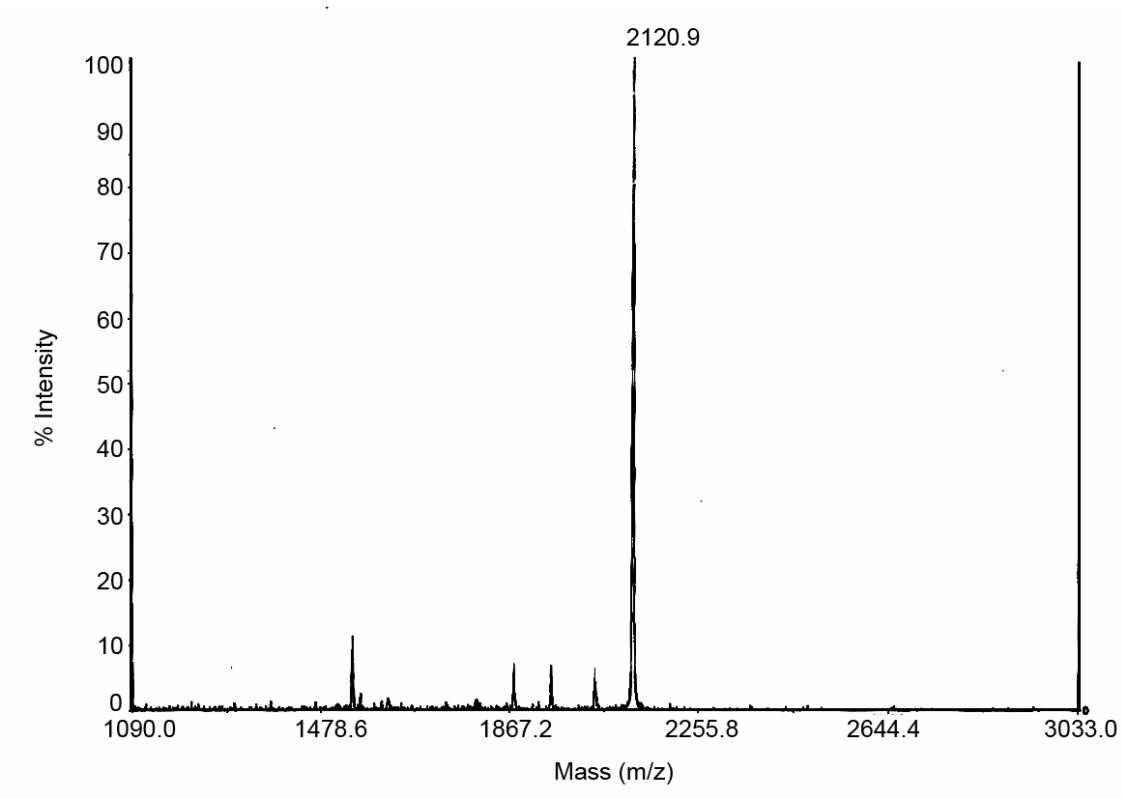


Fig. S 9 MALDI-TOF spectrum of **TAPA-a**

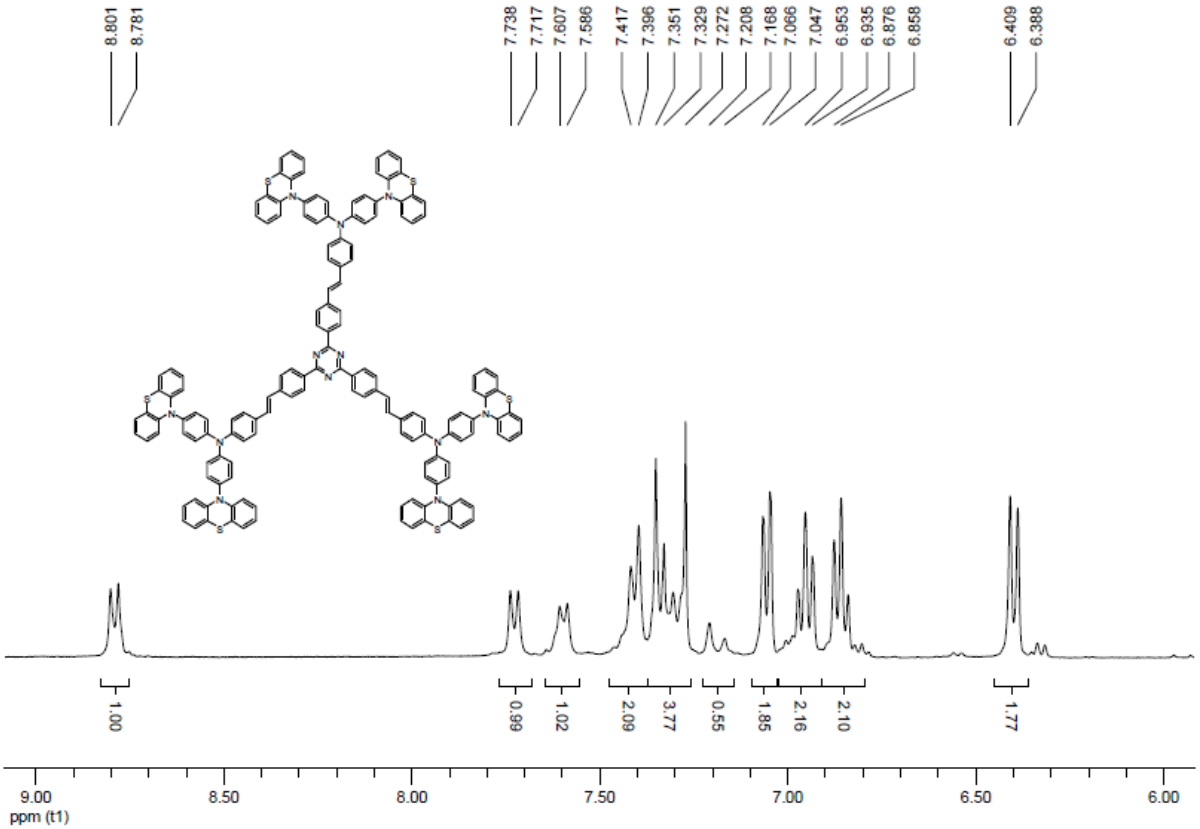


Fig. S 10 ^{1}H NMR spectrum of **TAPA-b** in chloroform-*d* (400 MHz)

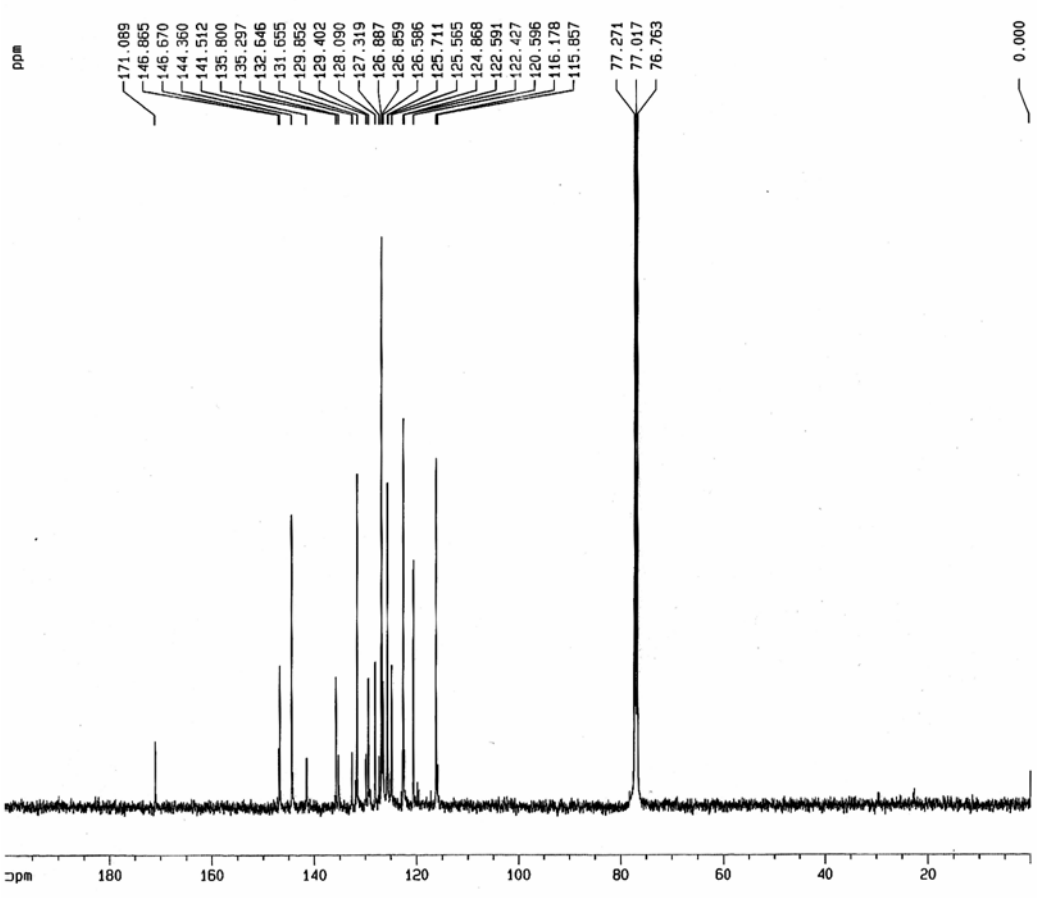


Fig. S 11 ^{13}C NMR spectrum of **TAPA-b** in chloroform-*d* (100MHz)

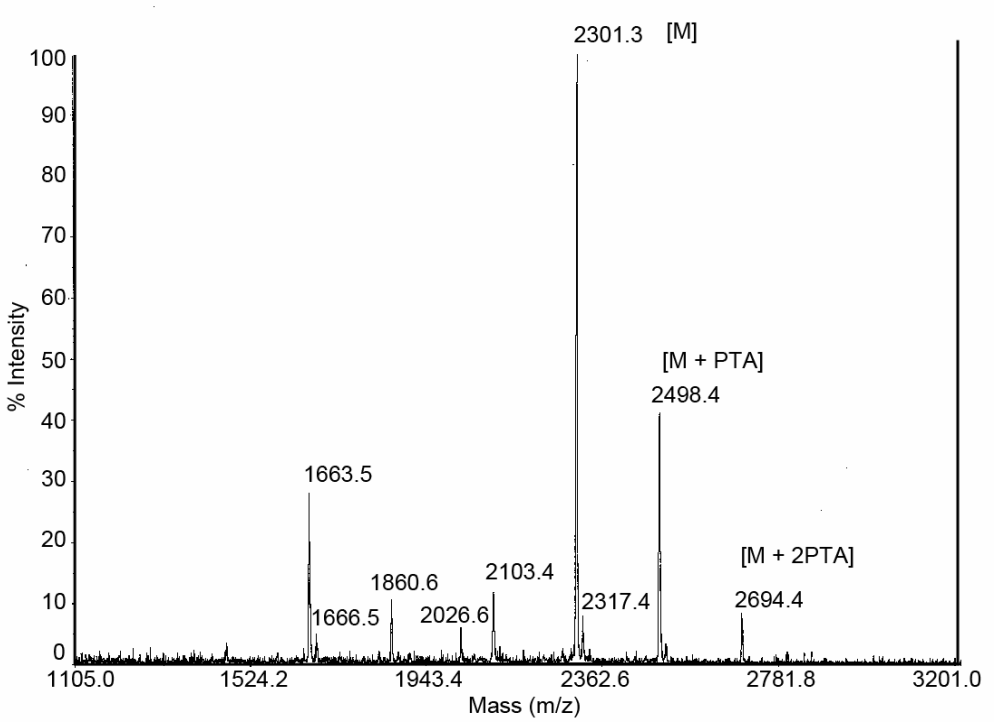


Fig. S12 MALDI-TOF spectrum of **TAPA-b** (PTA = Phenothiazine)

Reference

1. (a) F. Meng, B. Li, S. Qian, K. Chen and H. Tian, *Chem. Lett*., 2004, **33**, 470–471. (b) Z. J. Ning, Z. Chen, Q. Zhang, Y. L. Yan, S. X. Qian, Y. Cao, and H. Tian *Adv. Funct. Mater*., 2007, **17**, 3799–3807.
2. Y. H. Jiang, Y. C. Wang, J. L. Hua, S. Y. Qu, S. Q. Qian and H. Tian. *J. Polym. Sci., Part A.* 2009, **47**, 4400.
3. N. B. McKeown, S. Badriya, M. Helliwell and M. Shkunov; *J. Mater. Chem*., 2007, **17**, 2088–2094