Supporting information for

Fluorescent "glue" of water triggered by hydrogen-bonding cross-linking

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Materials and methods

All solvents and reagents used were reagent grade and were used without further purification unless otherwise stated. All organic solvents used to measures were dried before use. ^{1}H NMR and ^{13}C NMR were collected on a Bruker 500 avance III spectrometer. Mass spectrometric (MS) data were obtained with HP1100LC/MSD MS. Absorption and emission spectra were collected by using a Shimadzu 1750 UV-visible spectrometer and a RF-5301 fluorescence spectrometer (Japan), respectively. The microstructure of the samples was analyzed by field emission scanning electron microscopy (FESEM, S- 4800). Diameter distribution was obtained with Delsa Nano C analyzer (Beckman Coulter, Inc).

The common filter paper for humidity test, water-jet printing and fingerprint image was purchased from local company (Yangling reagent company, Shaanxi, China) and prepared with the size of 5 cm×5 cm. The concentration of **DMTA** dissolved in dry CH_2Cl_2 solution were increased from 0.04 to 10 mmol/L. Test strips were prepared by dipping the filter paper into above mentioned **DMTA** solution for 2 h and then dried in dry air for 10 s. RXZ artificial climate chamber (Jiangnan Instrument Factory, Ningbo, China) was used to produce and monitor humidity required. The relative humidity was fixed from 40% to 90%. Four different humidity values were used to simulate the humidity environment, then the filter paper treated with **DMTA** solution was put in the artificial climate chamber with given humidity value for three minutes. The optical images and fluorescent images excited by a hand-held UV lamp with excitation at 365 nm were observed by naked eye at room temperature.

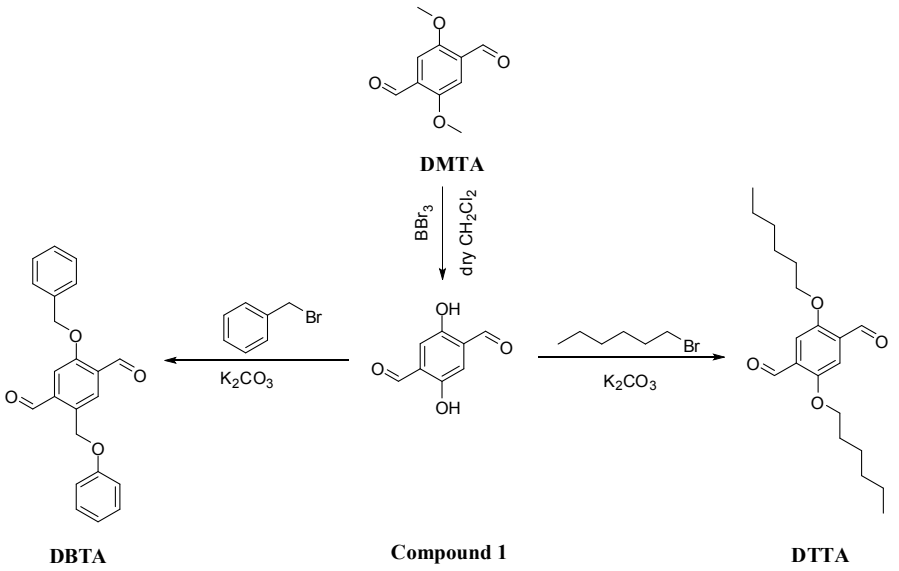
The samples for SEM experiments were obtained by applying a drop of **DMTA** solution with addition of different volume percentage of water in MeCN onto a silicon wafer followed by drying at room temperature.

The quantum yield of fluorescence of the sample was measured using quinine sulfate dissolved in 0.5 M H_2SO_4 ($\Phi = 0.55$) as a standard and calculated using eq 1:

$$\Phi_{unk} = \Phi_{std} \times \left(\frac{I_{unk}}{I_{std}}\right) \times \left(\frac{A_{std}}{A_{unk}}\right) \times \left(\frac{n_{unk}}{n_{std}}\right)^2 \quad (1)$$

The quantum yields of **DMTA** in MeCN, MeOH, DMF and THF in the absence of water are calculated to be 0.046, 0.18, 0.028 and 0.0072, respectively. Addition of water causes the quantum yields of **DMTA** to increase to 0.28 (25% in MeCN, v/v), 0.28 (35% in MeOH, v/v), 0.35 (80% in DMF, v/v) and 0.35 (90% in THF, v/v), respectively.

Synthesis



Scheme S1 Synthetic routine of **DTTA** and **DBTA**.

2,5-Bis(methoxy)benzene-1,4-dialdehyde (DMTA)

DMTA was obtained with a high yield according to a literature procedure.[S1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 2H), 7.44 (s, 2H), 3.93 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 189.25, 155.75, 129.15, 110.92, 56.24.

2,5-dihydroxyterephthalaldehyde (**Compound 1**)

A three-necked reactor equipped with a thermomcter was charged with 1.94 g (10 mmol) of **DBTA** and 100 mL of dichloromethane under a nitrogen stream to pepare a solution, which was cooled to -20^{0}C. After addition of 30.0 mmol (30.0 mmol) of boron tribromide dropwise to the solution, the mixture was stirred at -20^{0}C for 1 hour. Then, after the reaction mixture was stirred for another 6 hours at room temperature, 300 mL ice water was added to the reaction mixture, followed by extraction twice with 200 mL ethyl acetate. The organic layer was collected and dried over anhydrous. The solvent was evaporated from the filtrate under reduced pressure. The resulting solid was added to 50 mL of toluene. After stirring the mixture for 5 minutes, the resulting crystals were filtered off to obtain 1.2 g of Compound **1** as yellow crystals (yield: 61.8%).

2,5-bis(benzyloxy)terephthalaldehyde (DBTA)

A mixture of 2,5-dihydroxyterephthalaldehyde (1.65g, 10 mmol), benzyl bromide (5.13 g, 30 mmol) and K_2CO_3 (4.14 g, 30 mmol) in acetonitrile (50 mL) was heated to reflux for 12 hours. After cooling to room temperature, the precipitates were filtered, then evaporation of the solvent under reduced pressure. The solid residues were collected and purified on a silica gel column by using an eluent (petroleum ether), the product 5 was obtained as a yellow solid (2.42 g, 69.0% yield).^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 2H), 7.51 (s, 2H), 7.44-7.25 (m, 10H), 5.13 (s, 4H).^{13}C NMR (126 MHz, $CDCl_3$) δ 189.07, 155.05, 135.72, 129.61, 128.82, 128.51, 127.63, 112.45, 71.23. MS (ESI+) found 369.06 $(M+Na)^+$, calcd for $C_{22}H_{18}O_4Na$, 369.37.

2,5-bis(hexyloxy)terephthalaldehyde (DTTA)

The synthesis of the compound **DTTA** is similar to that of **DBTA** by using 1-bromine hexane to replace benzyl bromide. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 2H), 7.40 (s, 2H), 4.06 (t, J = 6.5 Hz, 4H), 1.81 (m, 4H), 1.53-1.39 (m, 4H), 1.38-1.27 (m, 8H), 0.89 (dd, J = 7.0, 4.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.43, 155.25, 129.30,

111.64, 69.27, 31.49, 29.03, 25.70, 22.58, 14.01. MS (ESI+) found 335.01 $(M+H)^+$, calcd for $C_{20}H_{31}O_4$, 335.22.

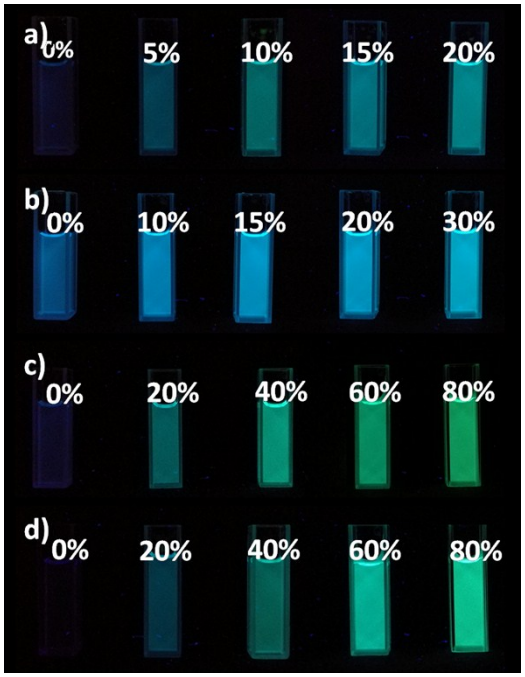


Fig. S1 Photographs of **DMTA** (10 μM) in the absence and presence of water in different solvents (a) MeCN, (b) MeOH, (c) DMF and (d) THF excited by a hand-held UV lamp with excitation at 365 nm, where percentages represent the water contents in solvents (v/v).

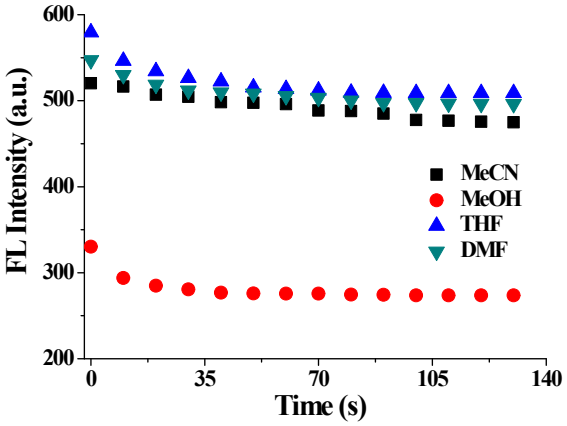


Fig. S2 The fluorescence intensity changes of **DMTA** at maximal fluorescence wavelength in different solvents containing water with duration time, where the waters contents are as follow: 25% in MeCN (v/v), 35% in MeOH (v/v), 90% in THF (v/v) and 80% in DMF (v/v), respectively.

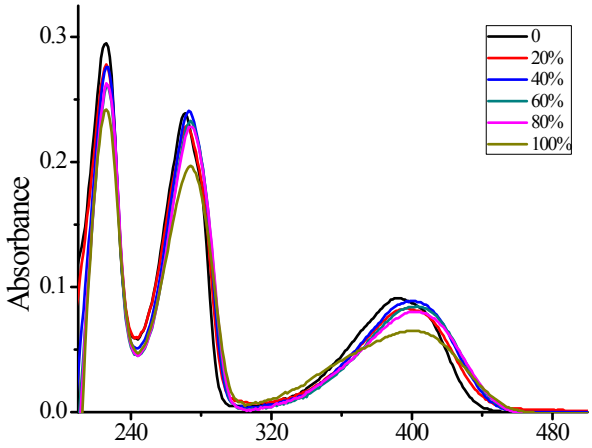


Fig. S3 Absorbance changes of **DMTA** (10 μM) in dry MeCN upon addition of water.

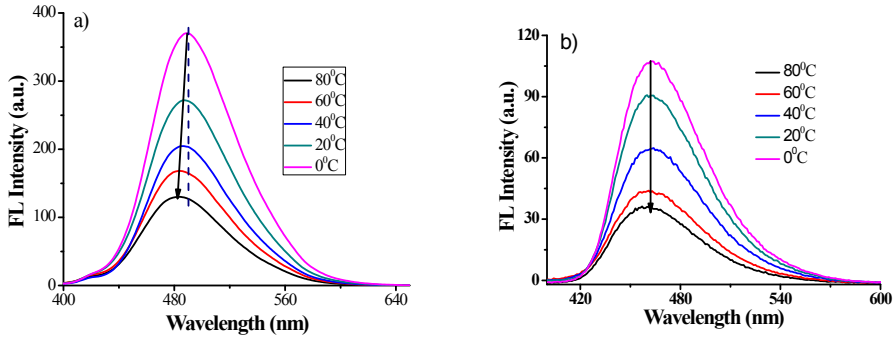


Fig. S4 The influence of temperature on the fluorescence spectra of **DMTA** (10 μM) in the (a) H_2O/MeCN (1:2, v/v) and (b) MeCN (λ_{ex} =390 nm, Slits: 3/3 nm).

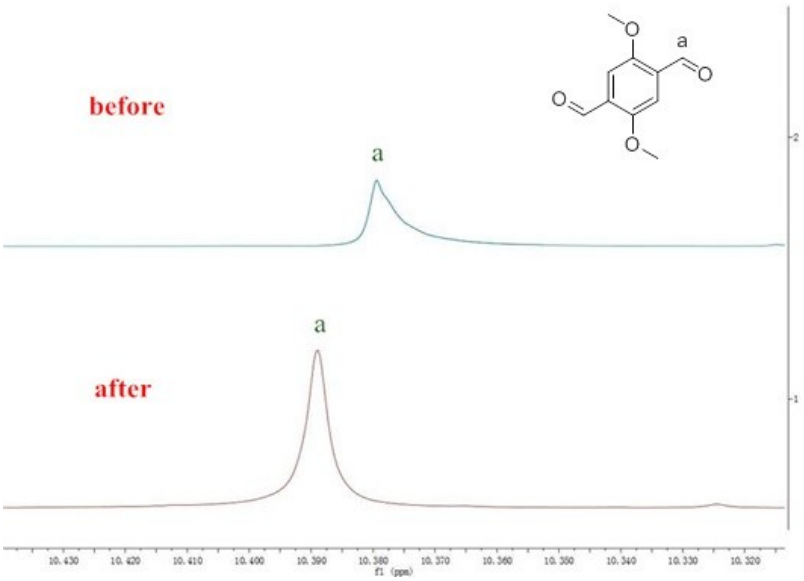


Fig. S5 Changes of chemical shift of H_a before and after addition of 5% water.

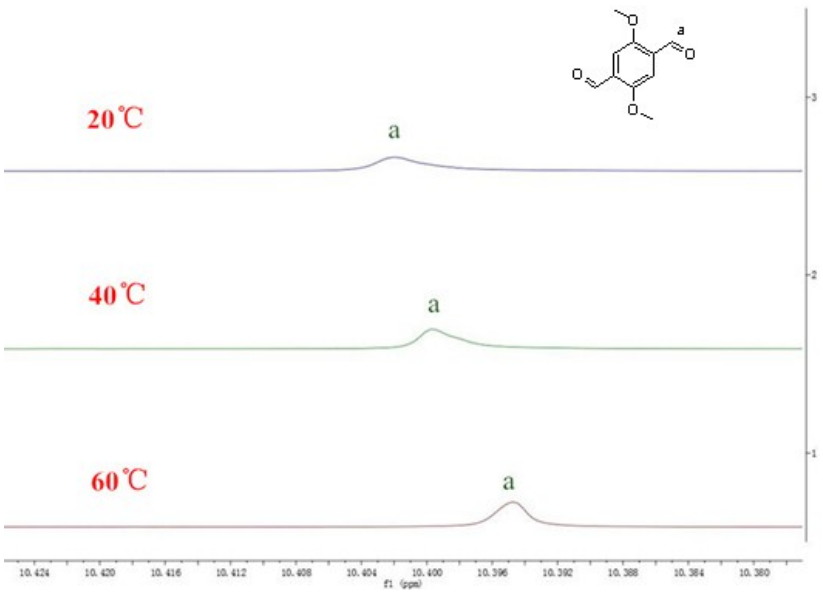


Fig. S6 Changes of chemical shift of H_a with different temperature.

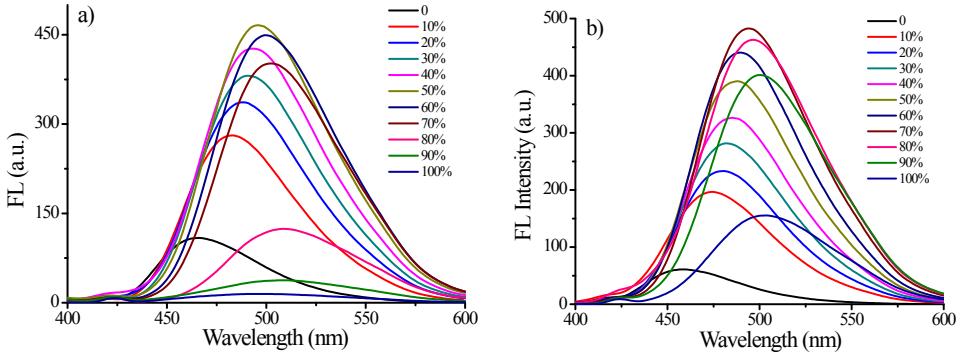


Fig. S7 Fluorescence spectral changes of **DTTA** (10 μM) (a) and **DBTA** (10 μM) (b) in dry MeCN treated with different volume percentage of water (λ_{ex} = 390 nm, Slits: 3/3 nm).

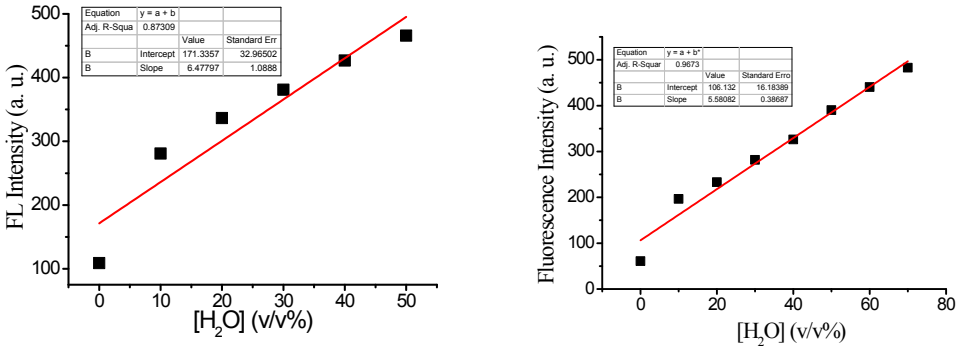


Fig. S8 Fluorescence intensity changes of **DTTA** (10 μM) (a) and **DBTA** (10 μM) (b) in dry MeCN treated with different volume percentage of water (λ_{ex} = 390 nm, Slits: 3/3 nm).

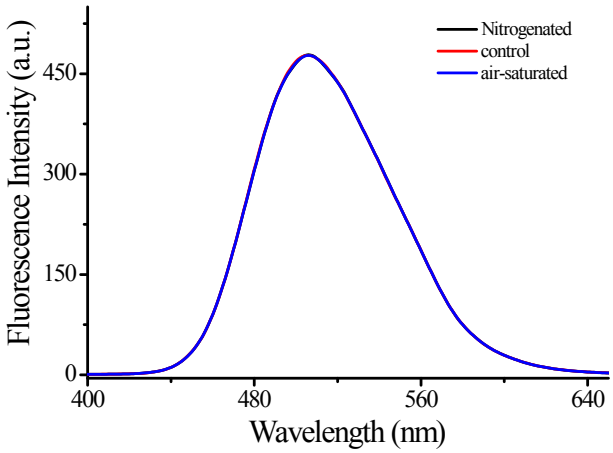


Fig. S9 The effects of dissolved oxygen on the fluorescence wavelength of **DMTA** (10 μM) in water (λ_{ex} =390 nm, Slits: 3/3 nm).

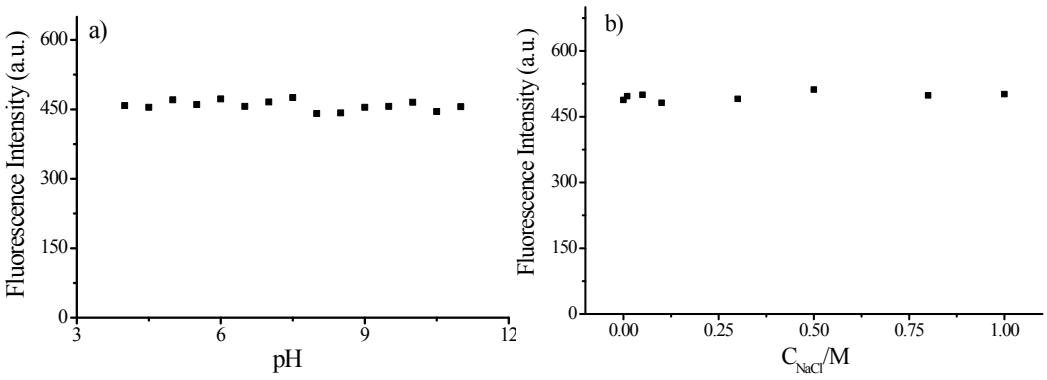


Fig. S10 The effects of (a) ionic strength and (b) pH on the fluorescence intensity at 506 nm of **DMTA** (10 μM) in water (λ_{ex} =390 nm, Slits: 3/3 nm).

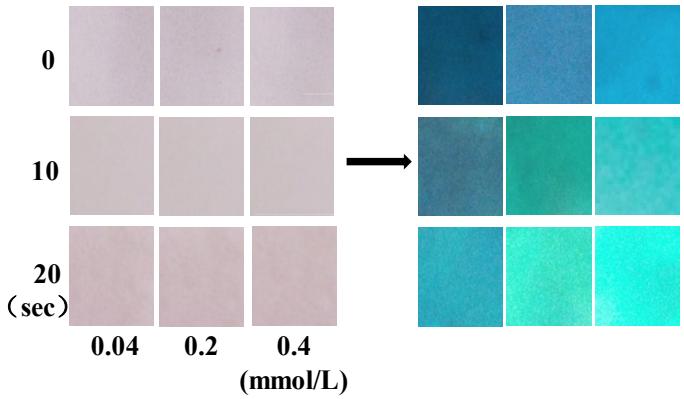


Fig. S11 The optical images (left) and fluorescent images (right) of **DMTA**-coated paper prepared from different concentration of the **DMTA** in CH_2Cl_2 under different treatment time of water-spraying. The fluorescent color changes were observed using a hand-held UV lamp with an excitation at 365 nm.

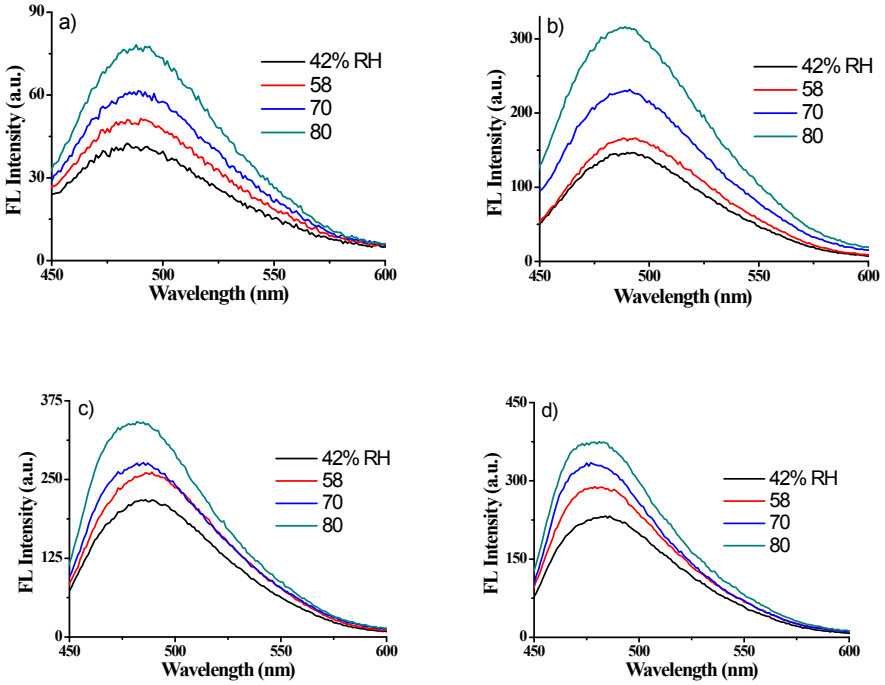


Fig. S12 The fluorescence spectra of **DMTA**-coated paper prepared from different concentration of **DMTA** in CH_2Cl_2 under chamber with different relative humidity (RH) values for three minutes (excitation at 390 nm), where the concentrations of **DMTA** are as follow: a) 0.04, b) 0.4, c) 4 and d) 10 mmol/L, respectively.

Fig. S13 The luminescent letters "Northwest A&F University" in size 5 were printed by water-jet printing with cartridges (HP 1010) refilled with water. (UV-Vis excitation at 254 nm a) and 365 nm b))

Fig. S14 The luminescent letters “water” written on **DMTA**-coated paper with a water-filled pen (UV-Vis excitation at 254 nm).

Fig. S15 The badge of Northwest A&F University printed with color laser-jet printing.

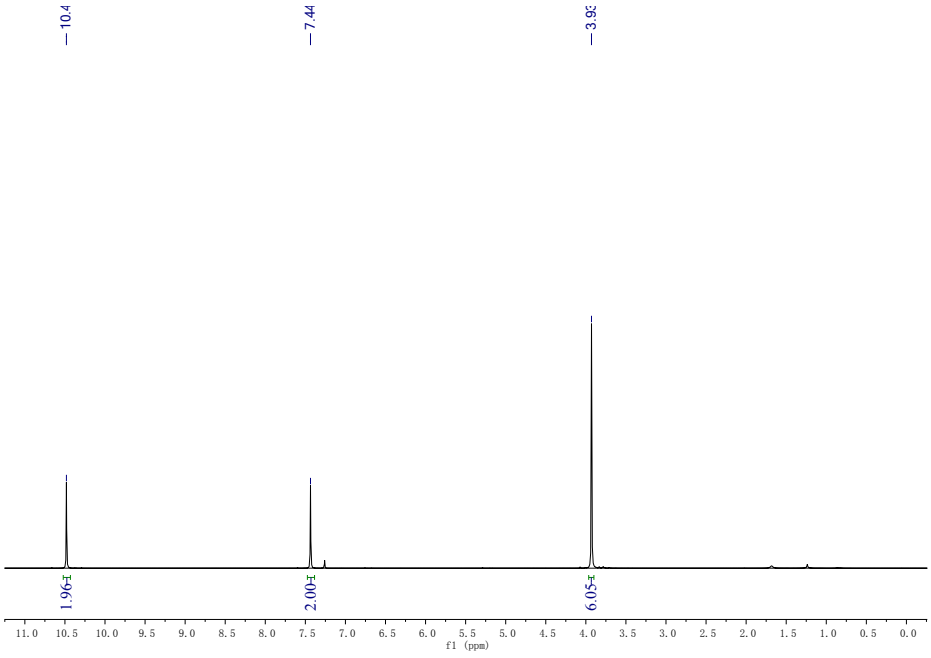


Fig. S16 ^{1}H NMR spectrum of **DMTA**.

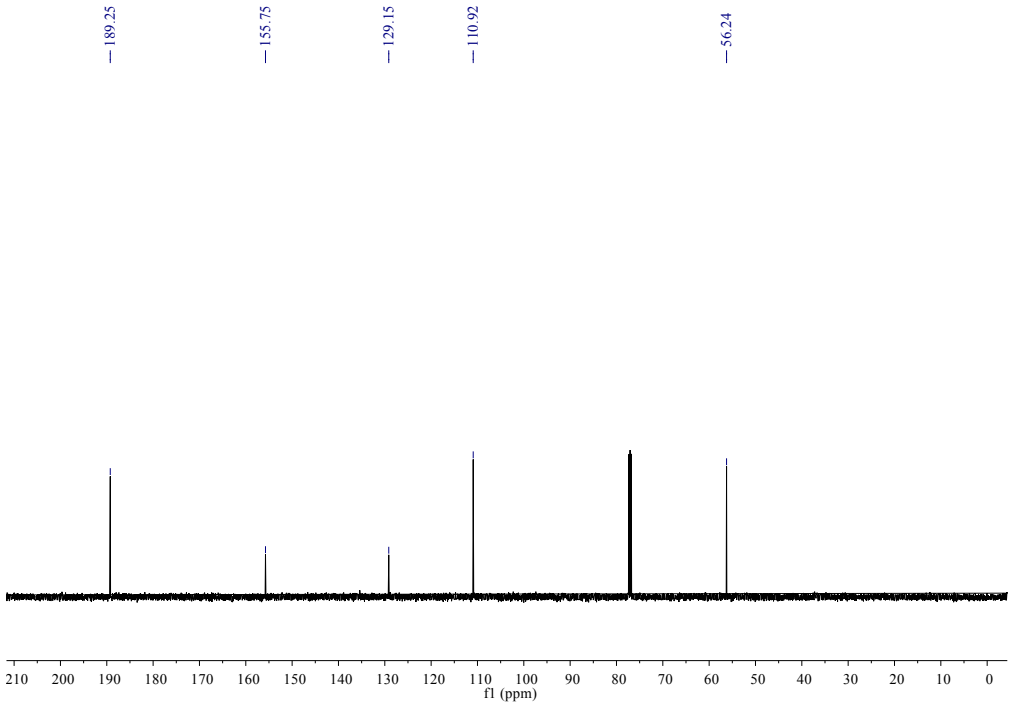


Fig. S17 ^{13}C NMR spectrum of **DMTA**.

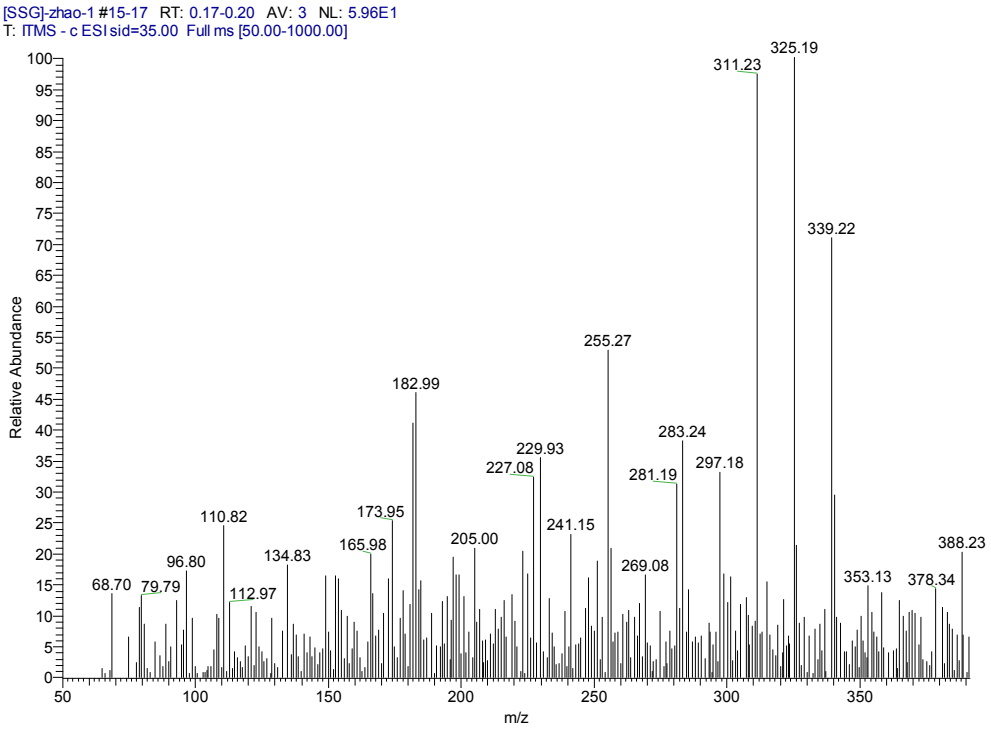


Fig. S18 MS of **DMTA**.

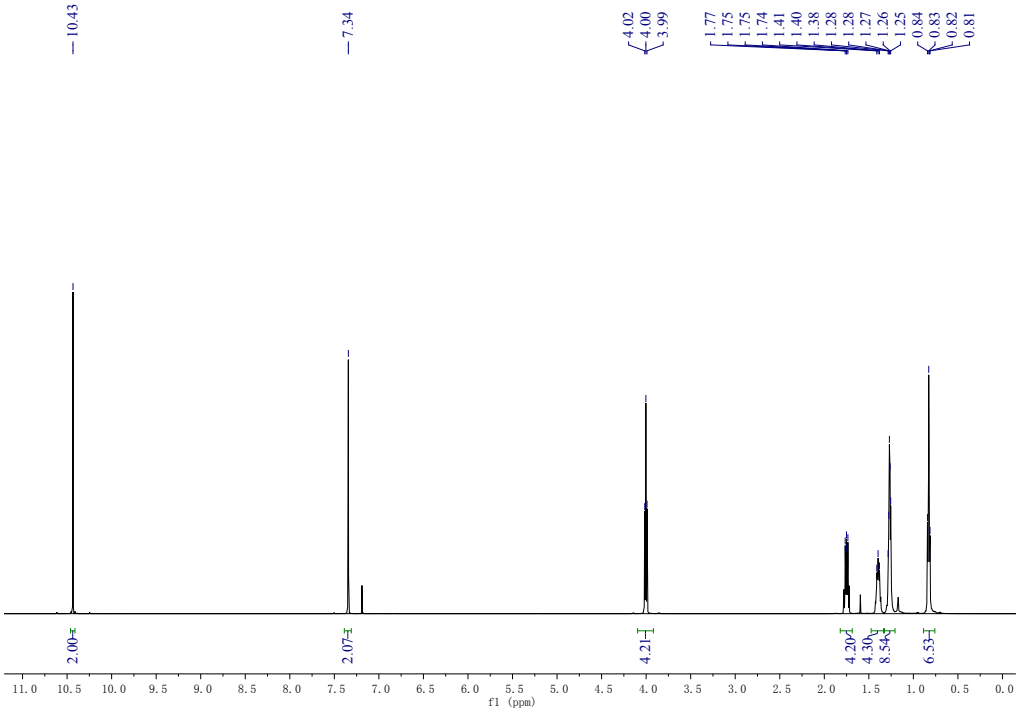


Fig. S19 ^{1}H NMR spectrum of **DTTA**.

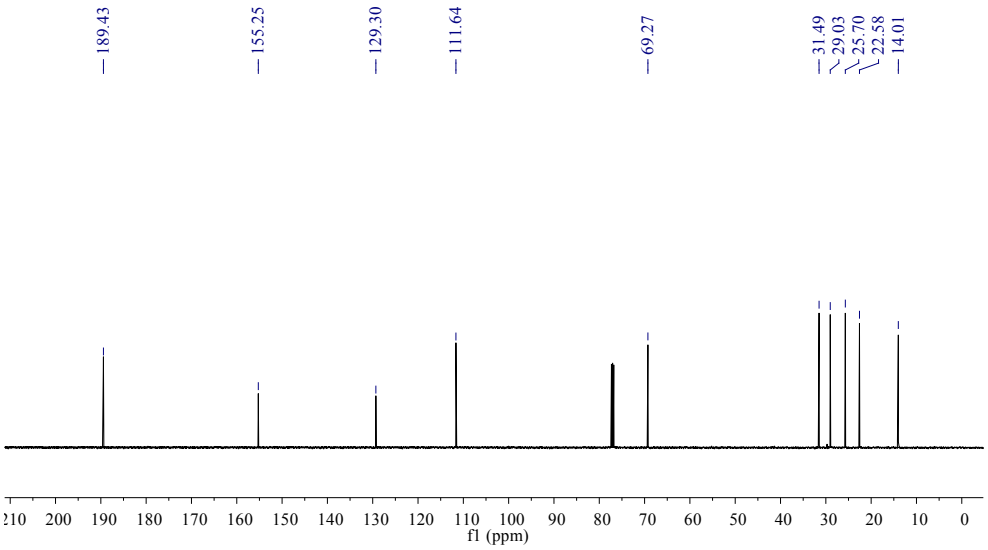


Fig. S20 ^{13}C NMR spectrum of **DTTA**.

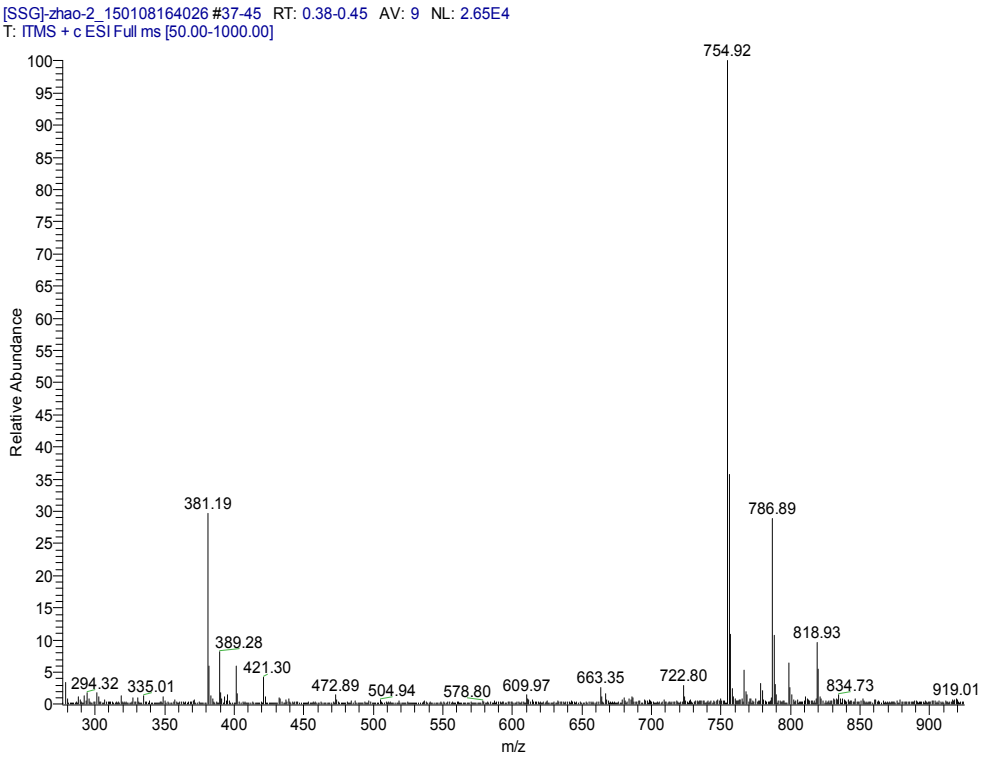


Fig. S21 MS of **DTTA**.

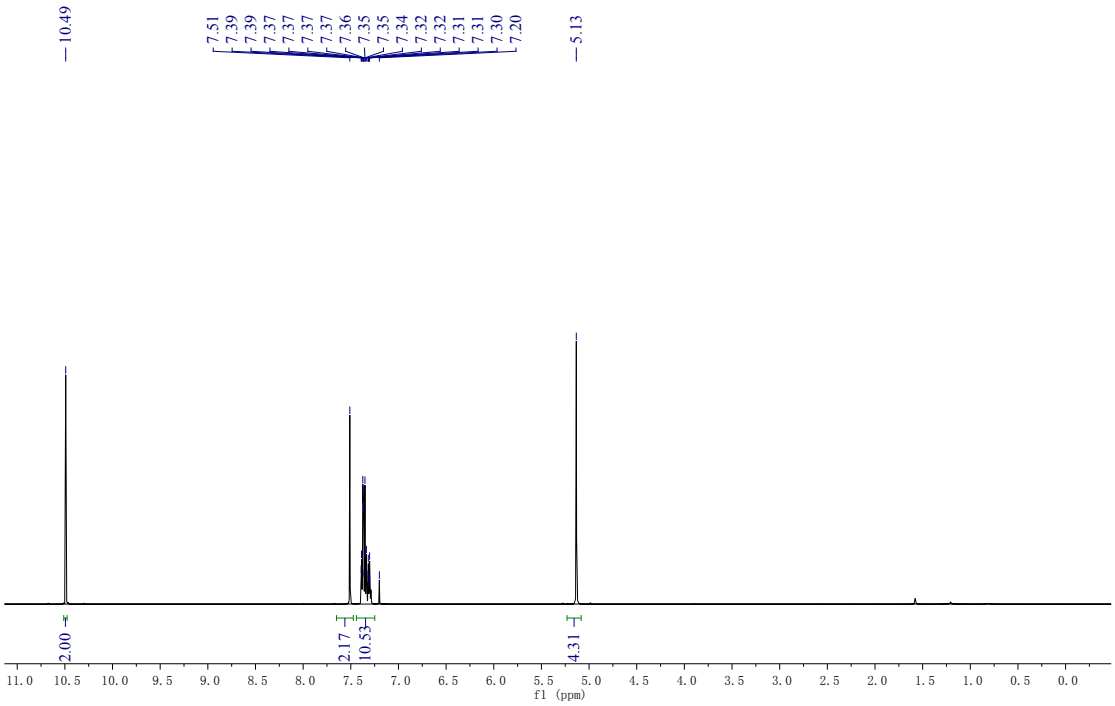


Fig. S22 ^{1}H NMR spectrum of **DBTA**.

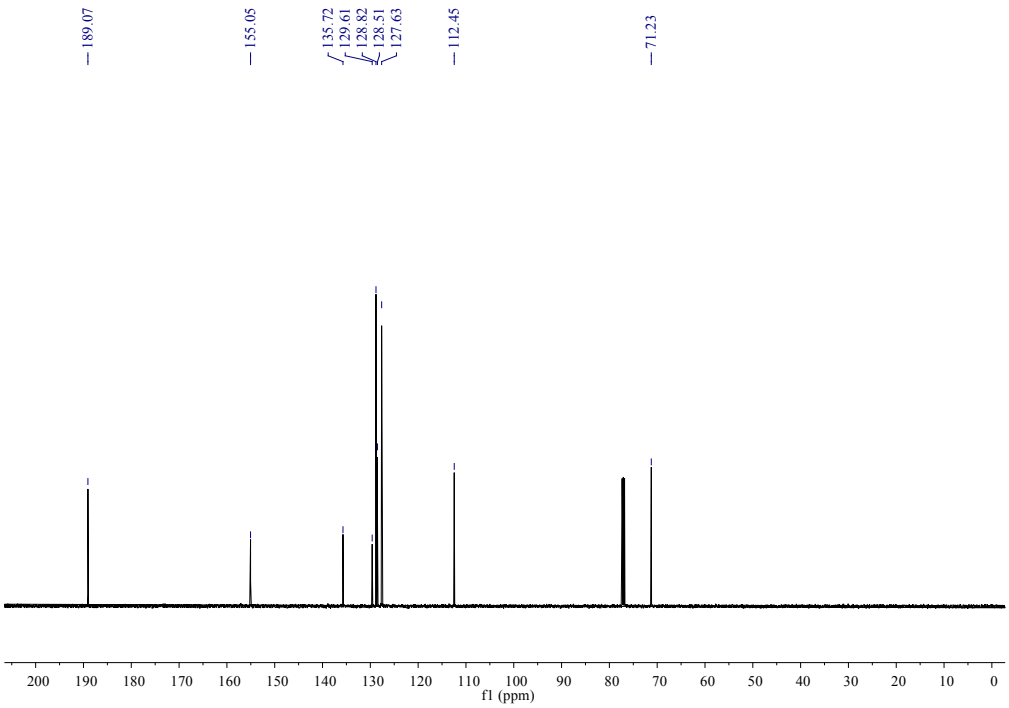


Fig. S23 ^{13}C NMR spectrum of **DBTA**.

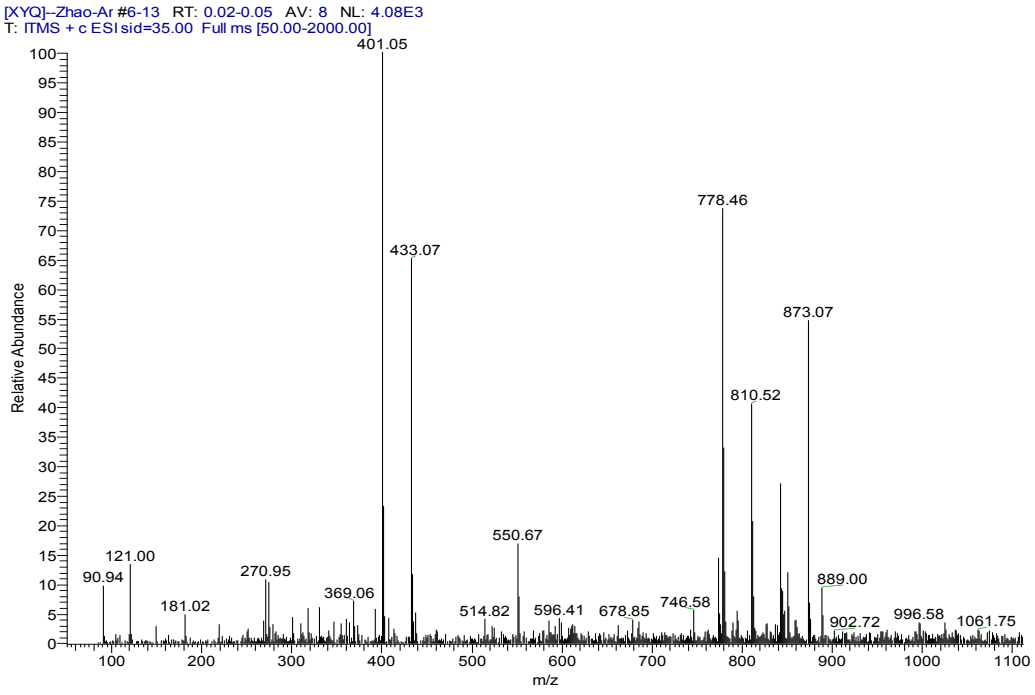


Fig. S24 MS of **DBTA**.

S1 P. Shao, Z. Li, J. Luo, H. Wang, and J. Qin, *Synth. Commun.*, 2005, **35**, 49-53.