

Supporting Information

Photopolymerization with AIE dyes for solid-state luminophores

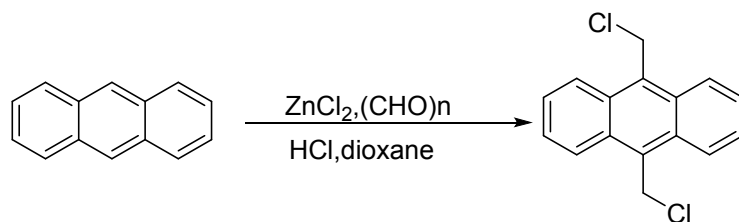
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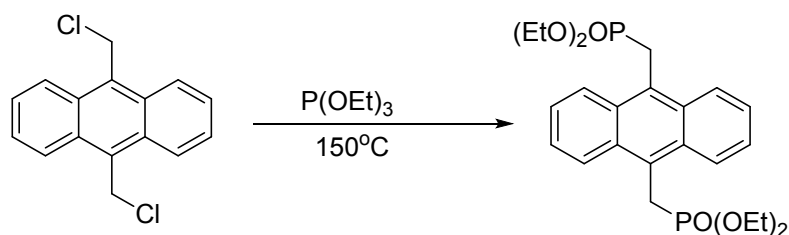
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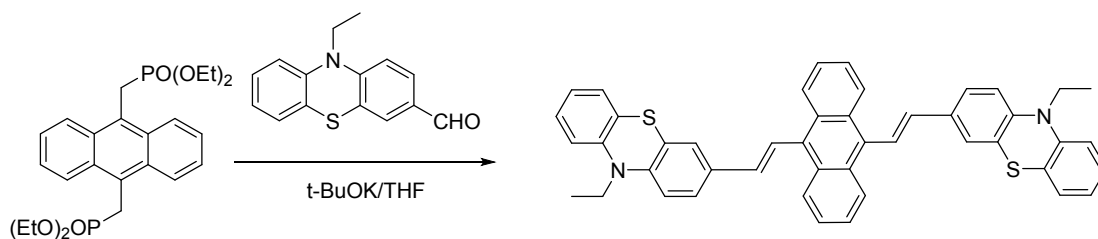
Synthesis



9, 10-bis(chloromethyl)anthracene (AnCl). 18.0 g (0.1 mol) of hydrazine, 15.2 g of paraformaldehyde, 144 mL of dioxane, 24 mL of concentrated hydrochloric acid were added to a 250 mL four-necked flask, and the mixture was heated to reflux with stirring. After refluxing for 8 hours, the reaction was followed by TLC. Cool to room temperature and filter. The filter cake was washed three times with dioxane (50 mL), washed with water until neutral, and finally rinsed once with dioxane. Drying to obtain a granulated yellow solid powder. Recrystallization from toluene gave 9,10-dichloromethylguanidine yellow needle crystals. $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 8.38 (m, 4H), 7.66 (m, 4H), 5.61 (s, 4H)

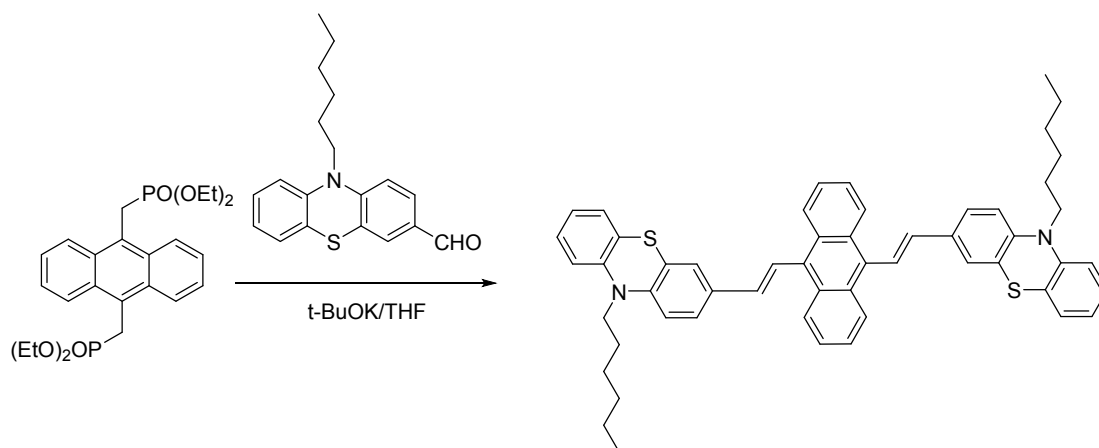


9,10-Bis(diethylphosphorylmethyl)anthracene (AnP). A solution of AnCl (10 g, 0.035 mol) and triethyl phosphite (100 mL, 0.48 mol) was stirred vigorously 4h at gentle reflux. The excess triethyl phosphate was removed by distillation under reduced pressure. The crude product was separated by silica gel column chromatography using ethyl acetate/petroleum ether (1/1, v/v) as the eluent. A yellow solid was obtained (14.43 g, 86.2%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 8.38-8.37 (m, 4H), 7.58-7.56 (m, 4H), 4.21 (d, 4H), 3.91-3.86 (m, 4H), 3.82-3.78 (m, 4H), 1.06 (t, 12H)



9,10-bis((E)-2-(10-ethyl-10H-phenothiazin-3-yl)vinyl)anthracene (MPA-E). AnP (1 g, 2.1 mmol), t-BuOK (1.9 g, 16.7 mmol), N-hexyloxazolaldehyde (1.18 g, 4.6 mmol), Into a 250 ml three-necked flask, nitrogen gas was exchanged three times, and then 100 ml of anhydrous tetrahydrofuran was added thereto, and the mixture was reacted at room temperature for 2 hours, and then heated to reflux for 6 hours. The reaction was followed by TLC (PE: EA = 3:1) until no starting material, and cooled. After adding 30 ml of methanol, the reaction was stirred for half an

hour, suction filtered, and the filter cake was washed three times with methanol, and a yellow solid was collected. ^1H NMR (400 MHz, CDCl_3) δ 8.34 – 8.21 (m, 4H), 7.71 (d, J = 16.6 Hz, 2H), 7.46 – 7.29 (m, 8H), 7.12 – 7.04 (m, 4H), 6.90 – 6.79 (m, 6H), 6.73 (d, J = 16.4 Hz, 2H), 4.01 – 3.82 (m, 4H), 1.41 (t, J = 6.9 Hz, 6H). FT-IR: 1598.09, 1574.93, 1493.38, 1463.78, 1405.68, 1329.15, 1281.70, 1246.78, 1133.57, 1068.93, 979.67, 793.36, 752.21, 675.12, 652.19, 607.00, 562.57. HRMS(ESI): 684.2113



9,10-bis((E)-2-(10-hexyl-10H-phenothiazin-3-yl)vinyl)anthracene (MPA-H). AnP(1 g, 2.1 mmol), t-BuOK (1.9 g, 16.7 mmol), N-hexyloxazolaldehyde (1.43 g, 4.6 mmol), Into a 250 ml three-necked flask, nitrogen gas was exchanged three times, and then 100 ml of anhydrous tetrahydrofuran was added thereto, and the mixture was reacted at room temperature for 2 hours, and then heated to reflux for 6 hours. The reaction was followed by TLC (PE: EA = 3:1) until no starting material, and cooled. After adding 30 ml of methanol, the reaction was stirred for half an hour, suction filtered, and the filter cake was washed three times with methanol, and a yellow solid was collected. ^1H NMR (400 MHz, CDCl_3) δ 8.40 (m, 4H), 7.81 (d, J = 16.4 Hz, 2H), 7.48 (m, 8H), 7.20 (m, 4H), 6.95 (m, 6H), 6.83 (d, J = 16.4 Hz, 2H), 3.92 (t, J = 7.1 Hz, 4H), 1.94 – 1.82 (m, 4H), 1.56 – 1.28 (m, 12H), 0.94 (t, J = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.97, 136.18, 132.66, 131.87, 129.61, 127.41, 126.49, 125.97, 125.18, 124.33, 123.40, 122.51, 115.42, 77.31, 77.05, 76.73, 47.57, 31.53, 26.91, 26.71, 22.66, 14.06. FTIR: 3059.49, 2954.90, 2921.05, 2850.68, 1595.20, 1491.00, 1463.13, 1377.42, 1331.64, 1285.84, 1201.40, 1029.46, 971.50, 816.00, 794.45, 758.98, 739.51, 699.32, 613.38. HRMS(ESI): 792.3550

UV absorption spectra of MPA-H in water/THF mixtures with different volume fractions of water

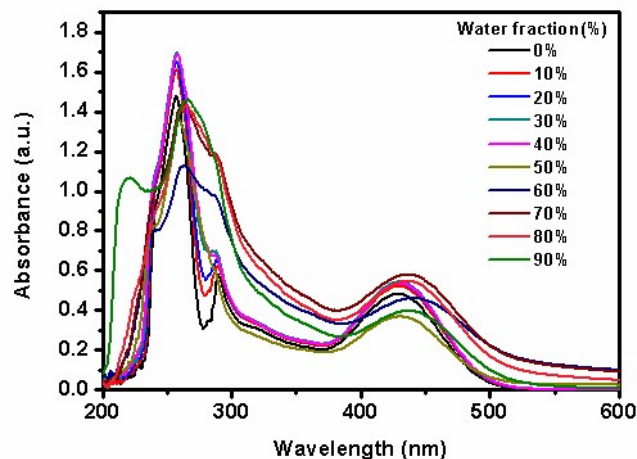


Fig S1 UV absorption spectra of MPA-H in water/THF mixtures with different volume fractions of water, concentration of MPA-H 2×10^{-5} mol/L.

Fluorescence change of the photopolymerization system

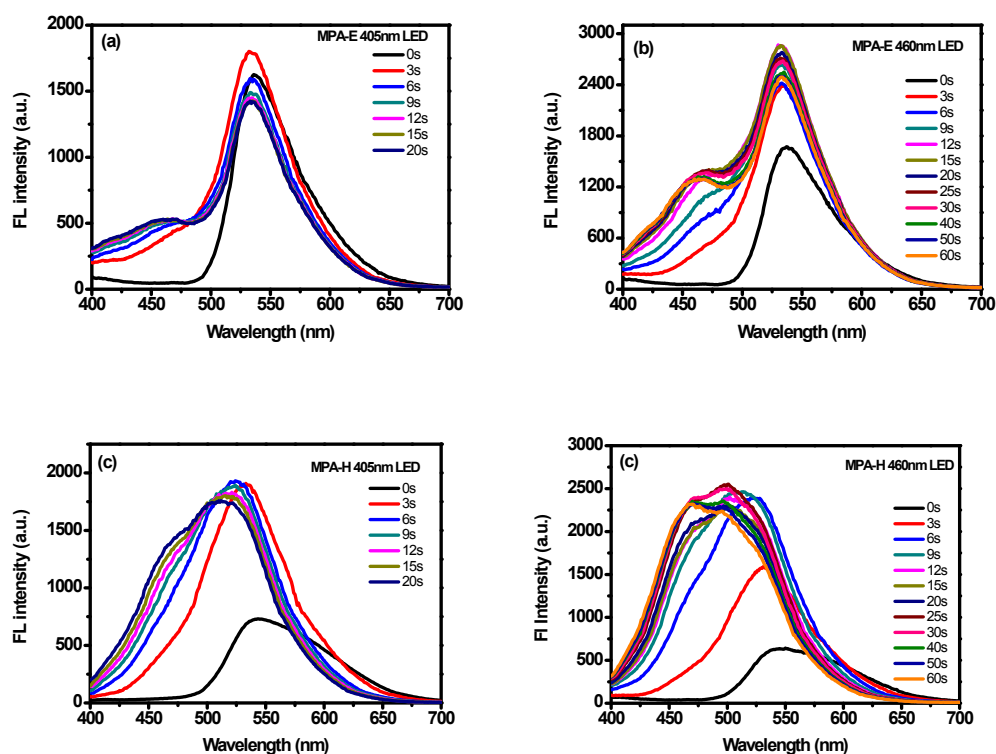


Fig S2 Changes of fluorescence spectra in photopolymerization of ETPTA initiated by MPAs/ iodonium salt under different LED sources: (a) MPA-E/ iodonium salt 405nm LED; (b) MPA-E/ iodonium salt 460nm LED; (c) MPA-H/ iodonium salt 405nm LED; (d) MPA-H/ iodonium salt 460nm LED

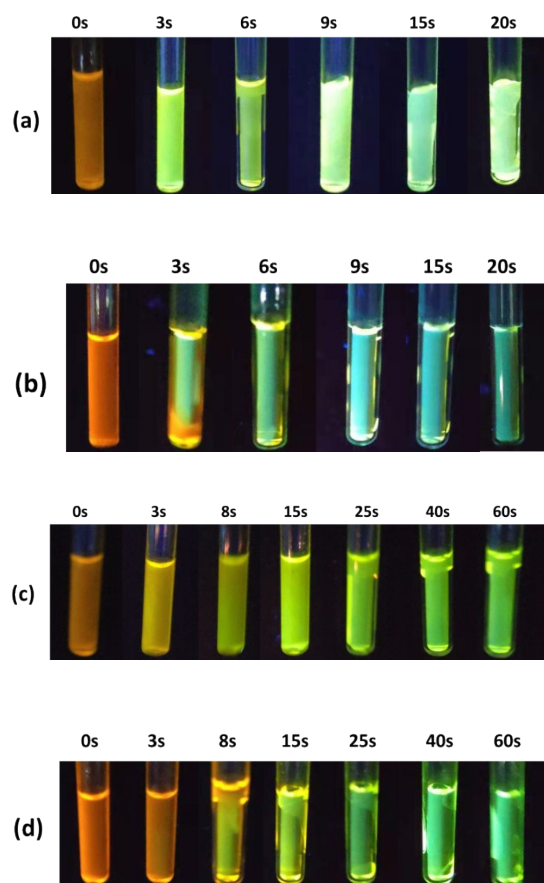


Fig S3 (a) Photograph of fluorescence changes during photopolymerization ETMPTA with MPA-E/ iodonium salt under 460nm LED; (b) Photograph of fluorescence changes during photopolymerization ETMPTA with MPA-H/ iodonium salt under 460nm LED; (c) Photograph of fluorescence changes during photopolymerization ETMPTA with MPA-E/ iodonium salt under 520nm LED; (d) Photograph of fluorescence changes during photopolymerization ETMPTA with MPA-H/ iodonium salt under 520nm LED

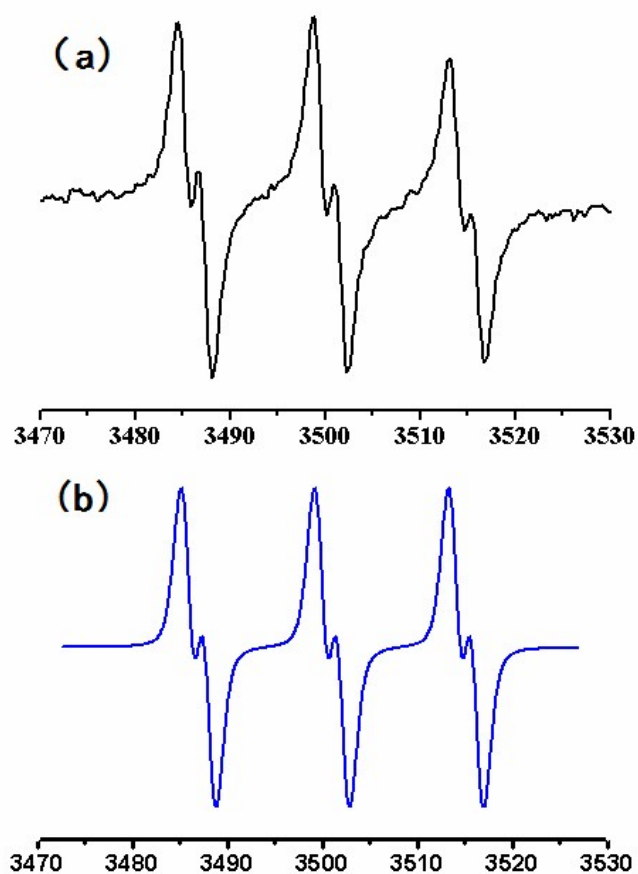


Fig S4 EPR spectra of radical generated in MPA-H/ iodonium salt and trapped by PBN in tert-butylbenzene ([Iodonium salt] = 0.01 M). (a) experimental and (b) simulated spectra. PBN/free radical adducts: MPA-H/ iodonium salt $a_N = 14.1$ G; $a_H = 2.00$ G.

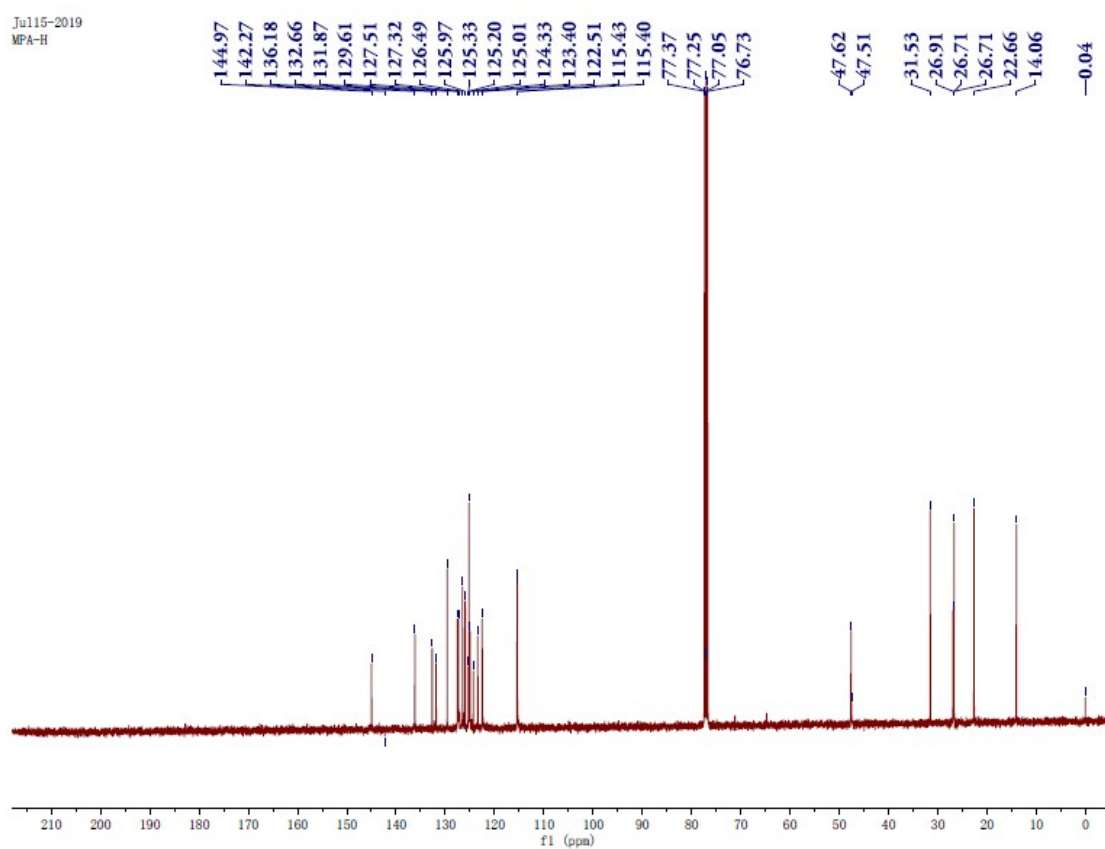
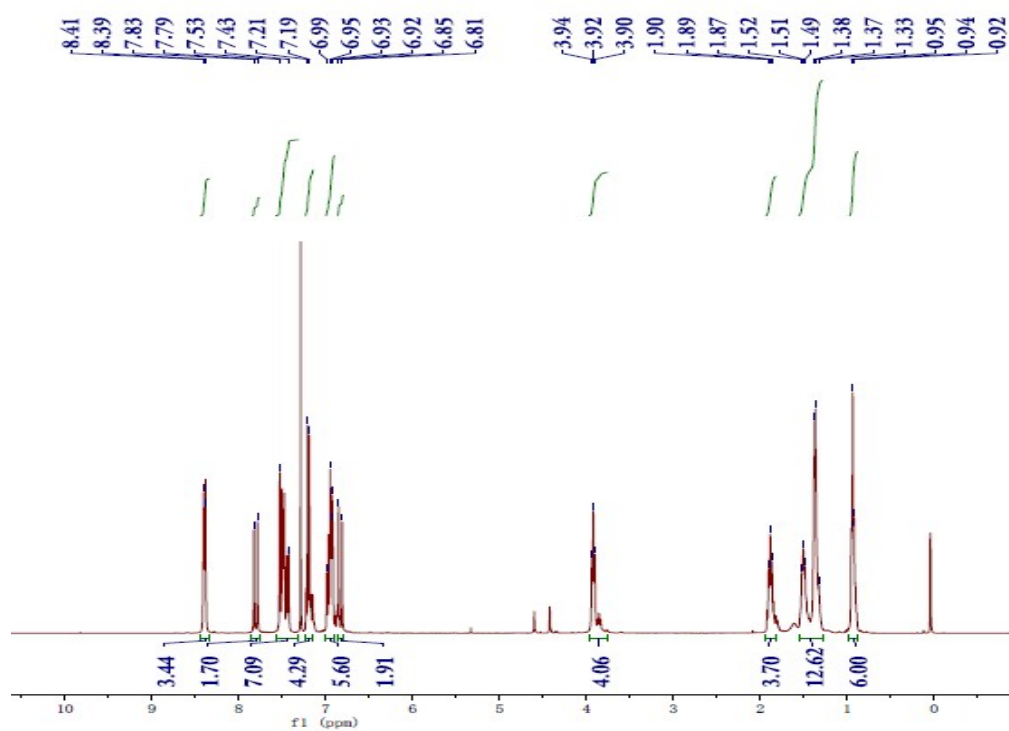


Fig S5 The ¹H NMR and ¹³C NMR spectra of MPA-H

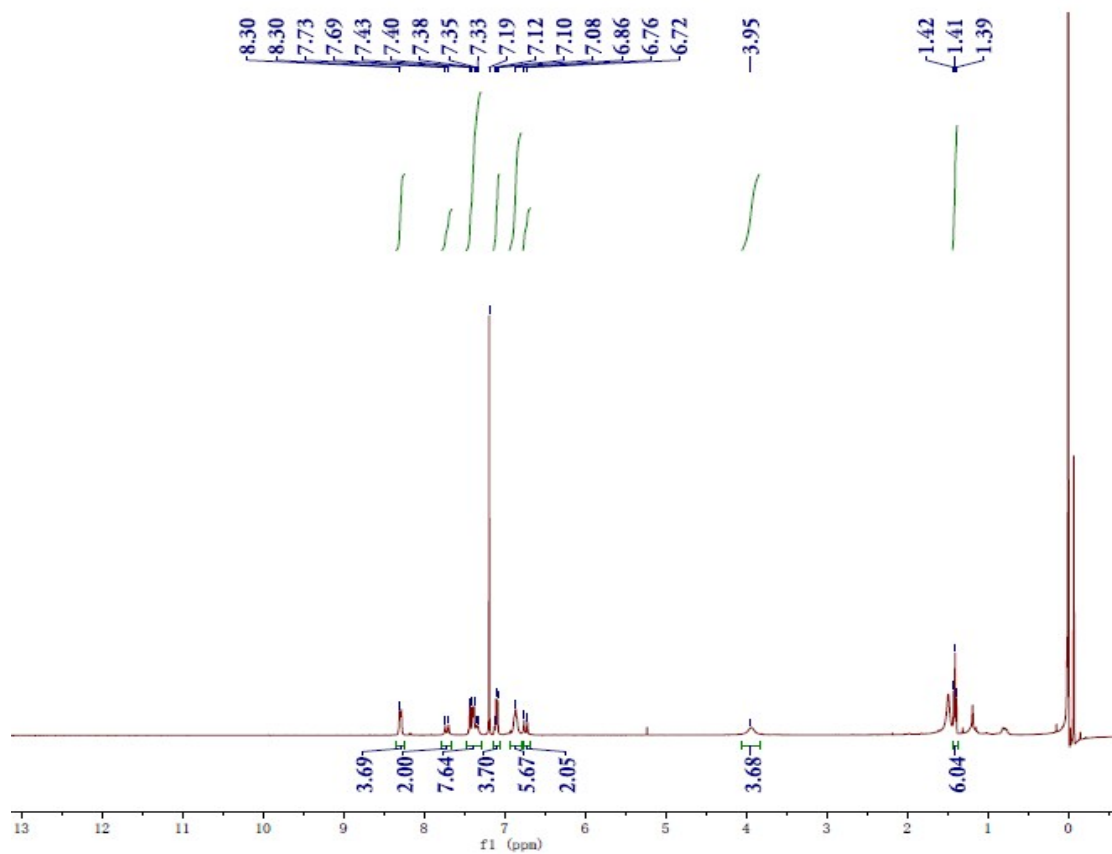


Fig S6 the ^1H NMR spectra of MPA-E