Supporting Information

D-A-D Type High Contrast Mechanochromic Luminescence Based on Anthracene and Pyridinium Salt Derivatives

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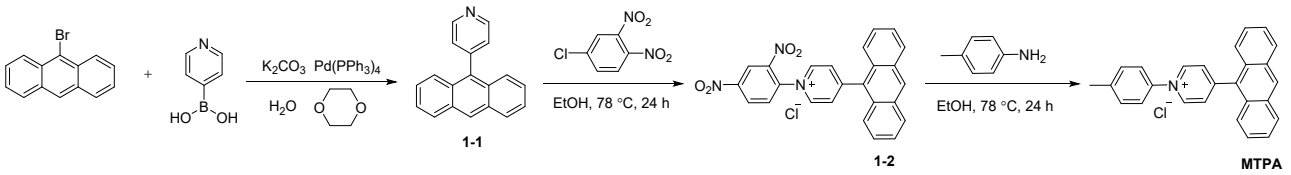
General Experimental Section.

The compounds and the reagents purchased from commercial suppliers were used without further purification. ^{1}H NMR spectra were measured on Bruker 400 MHz NMR spectrometer. Fluorescence spectra were recorded on F-4600. UV/Vis experiments were carried out with a TU-1810 instrument with 1 cm pathlength cells at 298 K. Powder X-ray diffraction (PXRD) were measured on A Rigaku Ultima IV X-Ray diffractometer with graphite-monochromated Cu Kα radiation in the 2θ range of 5–50°.

Synthesis and characterization

Synthesis of MTPA



Scheme S1. Synthesis of MTPA.

Synthesis of ***1-1, 1-2*** and ***MTPA*** were adapted and modified from previously reported procedures.[1, 2, 3]

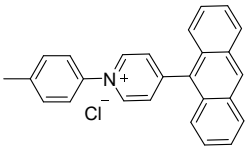
General procedure:

1-1: 9-Bromoanthracene (1.2857 g, 5 mmol)、Pyridine-4-boronic acid (0.9834 g, 8 mmol)、Tetrakis(triphenylphosphine)palladium (0.1965 g, 0. 17 mmol), and Potassium carbonate (1.2438 g, 9 mmol) were added in 1,4-Dioxane (20 ml) and distilled water (20 mL) was heated to refluxed for 24 h. Cool the reaction solution to room temperature and remove the solvent by vacuum distillation to obtain a viscous yellow liquid. Subsequently, extract the crude product 3 to 4 times with saturated sodium carbonate (Na_2CO_3) aqueous solution and dichloromethane (CH_2Cl_2). Collect the organic phase, dry it with anhydrous magnesium sulfate ($MgSO_4$) for 2 h, filter to collect the filtrate, and remove the solvent by vacuum distillation to obtain the crude product. Perform column chromatography for separation and purification (CH_2Cl_2/MeOH: 200/1), collect the sample, and remove the solvent by vacuum distillation to obtain yellow solid powder compound **1-1** (0.8809 g, 69 %).

1-2: Compound **1-1** (0.3064 g, 1.2 mmol) and 2,4-dinitrochlorobenzene (0.6077 g, 3 mmol) were added to a 100 mL round-bottom flask. Add 30 mL of ethanol (EtOH) and heat the mixture to 80 ℃ under nitrogen protection. After refluxing for 24 h, cool the reaction solution to room temperature, collect the solid sample by centrifugation, and wash it with ethanol (EtOH) 3 to 4 times. Finally, vacuum dry it to obtain the red solid powder compound **1-2** (0.4670 g, 85 %).

MTPA: Compound **1-2** (0.1282 g, 0.28 mmol) and p-toluidine (0.0750 g, 0.7 mmol) were added to a 100 mL round-bottom flask. Twenty milliliters of anhydrous ethanol (EtOH) solution was then added, and the mixture was heated to 80 ℃ under nitrogen protection. After refluxing for 24 hours, the reaction solution was cooled to room temperature. The solid sample was collected by centrifugation and washed with ethanol (EtOH) 3 to 4 times. Finally, it was vacuum-dried to obtain the red solid powder compound **MTPA** (0.0947 g, 85%).

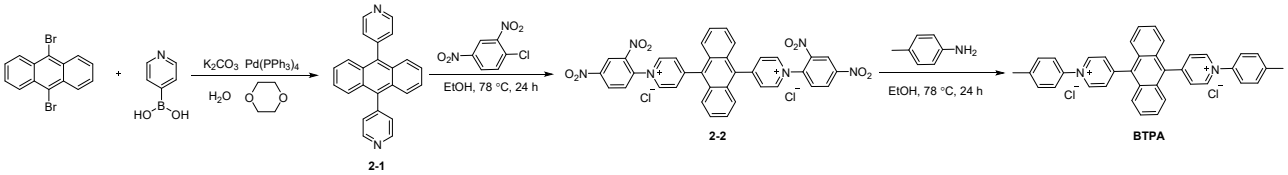
Characterization of B-1



MTPA

^{1}H NMR (400 MHz, D_2O) δ 9.22 (d, J = 6.7 Hz, 2H), 8.75 (s, 1H), 8.36 – 8.08 (m, 4H), 7.71 (d, J = 8.4 Hz, 2H), 7.57 (q, J = 7.2 Hz, 8H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 156.78, 144.93, 141.50, 140.64, 130.71 (d, J = 4.6 Hz), 130.32, 129.37, 128.93, 128.63, 127.36, 126.01, 125.20, 124.66, 20.86.

Synthesis of BTPA



Scheme S2. Synthesis of BTPA.

Synthesis of ***2-1***, ***2-1*** and ***BTPA*** were adapted and modified from previously reported procedures.[4]

General procedure:

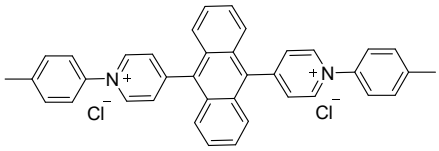
2-1: 9,10-Dibromoanthracene (1.6802g, 5 mmol)、Pyridine-4-boronic acid (2.2125g, 18 mmol)、Tetrakis(triphenylphosphine)palladium (0.3813g, 0. 33 mmol), and Potassium carbonate (2.5983g, 18.8 mmol) were added in 1,4-Dioxane (40 ml) and distilled water (20 mL) was heated to refluxed for 24 h. Cool the reaction solution to room temperature and remove the solvent by vacuum distillation to obtain a viscous yellow liquid. Subsequently, extract the crude product 3 to 4 times with saturated sodium carbonate (Na_2CO_3) aqueous solution and dichloromethane (CH_2Cl_2). Collect the organic phase, dry it with anhydrous magnesium sulfate ($MgSO_4$) for 2 h, filter to collect the filtrate, and remove the solvent by vacuum distillation to obtain the crude product. Perform column chromatography for separation and purification (CH_2Cl_2/MeOH: 150/1), collect the sample, and remove the solvent by vacuum distillation to obtain yellow solid powder compound **2-1** (1.1 g, 66.3 %).

2-2: Compound **2-1** (0.3986g, 1.2 mmol) and 2,4-dinitrochlorobenzene (1.2153g, 6 mmol) were added to a 100 mL round-bottom flask. Add 40 mL of ethanol (EtOH) and heat the mixture to 80 ℃ under nitrogen protection. After refluxing for 24 h, cool the reaction solution to room temperature, collect the solid sample by centrifugation, and wash it with ethanol (EtOH) 3 to 4 times. Finally, vacuum dry it to obtain the red solid powder compound **2-2** (0.7257 g, 82 %).

BTPA: Compound **2-2** (0.1865g, 0.28 mmol) and p-toluidine (0.1499g, 1.4 mmol) were added to a 100 mL round-bottom flask. Twenty milliliters of anhydrous ethanol (EtOH) solution was then added, and the mixture was heated to 80 ℃ under nitrogen protection.

After refluxing for 24 hours, the reaction solution was cooled to room temperature. The solid sample was collected by centrifugation and washed with ethanol (EtOH) 3 to 4 times. Finally, it was vacuum-dried to obtain the red solid powder compound **BTPA** (0.1400 g, 81%).

Characterization of BTPA



BTPA

^{1}H NMR (600 MHz, D2O) δ 9.40 (d, J = 6.0 Hz, 4H), 8.47 (d, J = 6.1 Hz, 4H), 7.84 (d, J = 8.0 Hz, 4H), 7.81 – 7.73 (m, 4H), 7.73 – 7.60 (m, 8H), 2.56 (s, 6H).

Photophysical properties of compounds MTPA and BTPA

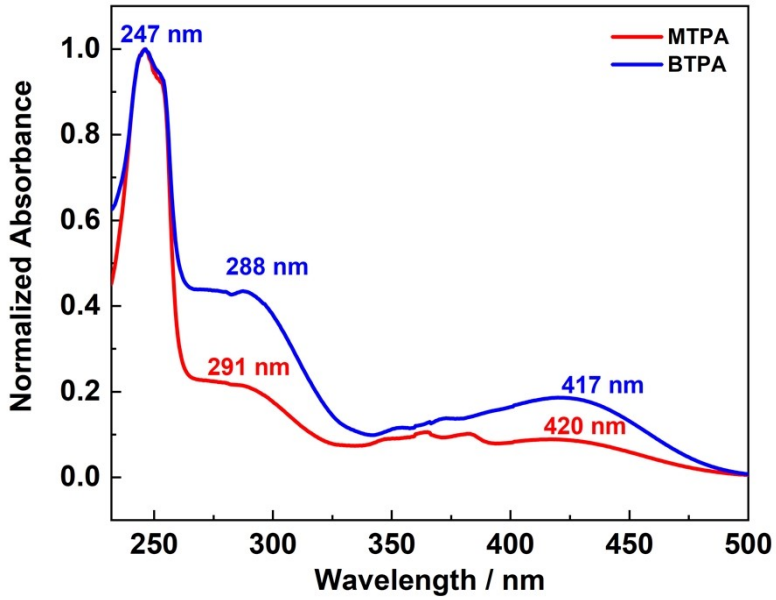


Figure S1 The normalized UV-vis absorption of compound **MTPA** and **BTPA** in H_2O recorded at room temperature.

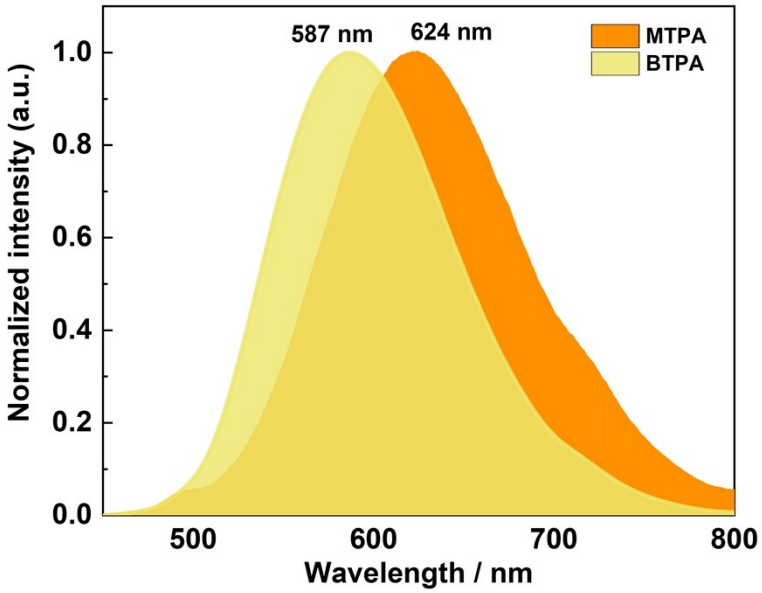


Figure S2 The normalized emission spectra of compound **MTPA** and **BTPA** in H_2O recorded at room temperature (λex = 420 nm).

Table S1 Photoluminescence data of **MTPA** and **BTPA** in states at room temperature

	λ_{em}/nm	τ/ns	φ_F/%
MTPA	450	1.46	4.57
MTPA Ground	572	7.06	1.97
BTPA	550	3.51	14.8
BTPA Ground	570	5.13	13.4

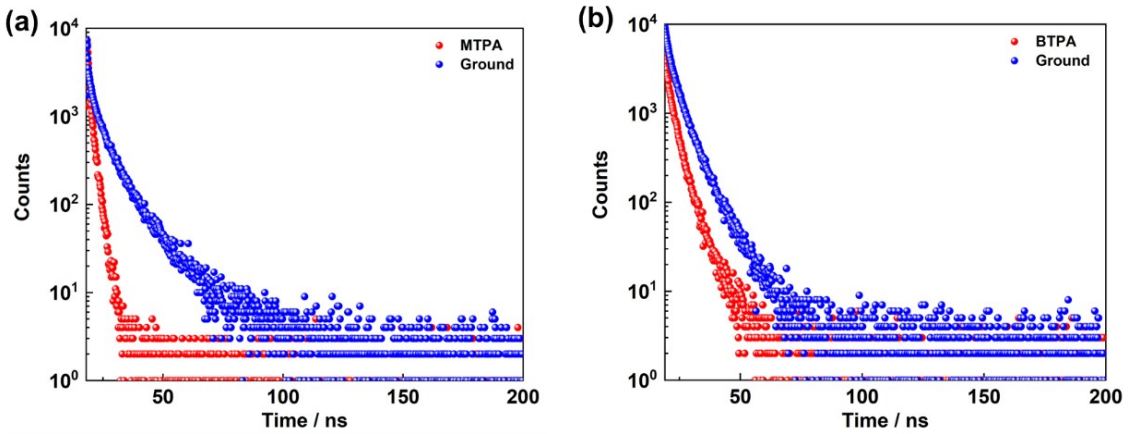


Figure S3 Time-correlated single photon counting decay profiles for the as-prepared and ground solids of **MTPA** (a) and **BTPA** (b).

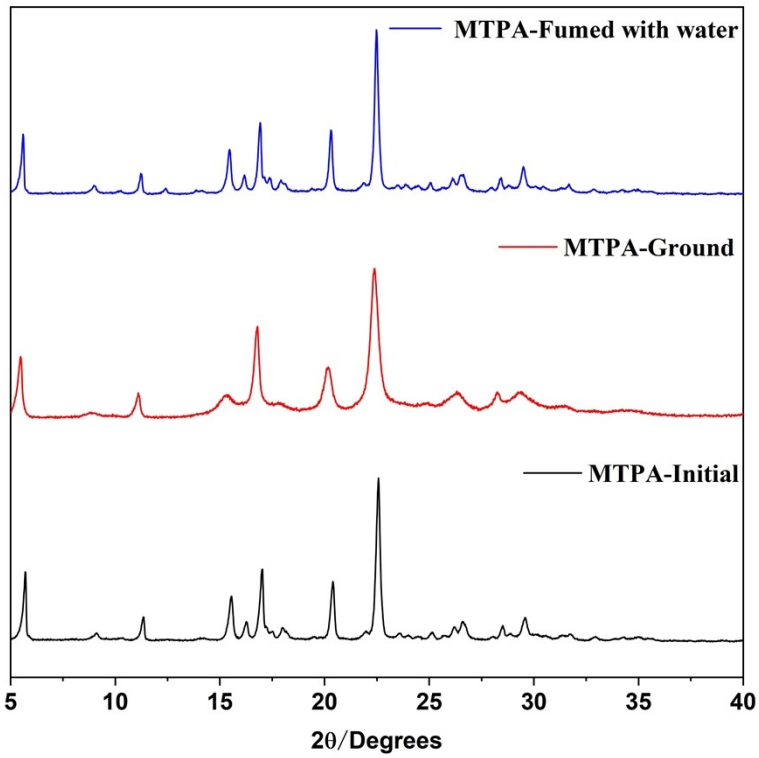


Figure S4 Powder X-ray diffraction (PXRD) patterns recorded the as-prepared and ground solids of **MTPA**.

Powder X-ray diffraction (PXRD) the as-prepared and ground solids of MTPA and BTPA

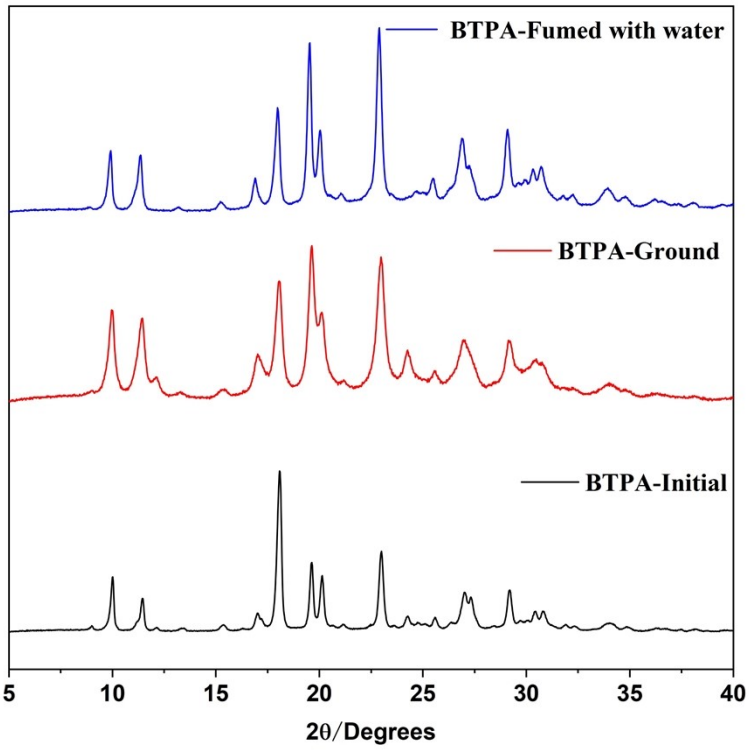


Figure S5 Powder X-ray diffraction (PXRD) patterns recorded the as-prepared and ground solids of **BTPA**.

^{1}H NMR spectra of 1-1, 1-2, MTPA, 2-1, 2-2, BTPA

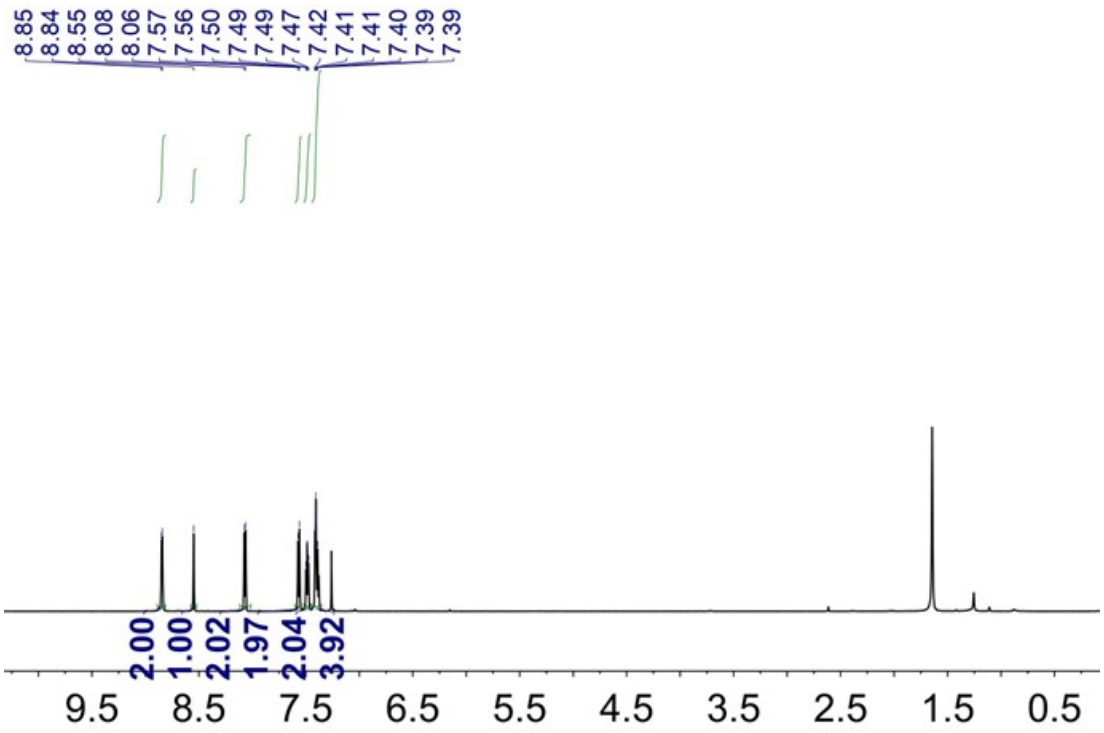


Figure S6 The ^{1}H NMR spectrum of compound **1-1** (400 MHz, $CDCl_3$, 298 k).

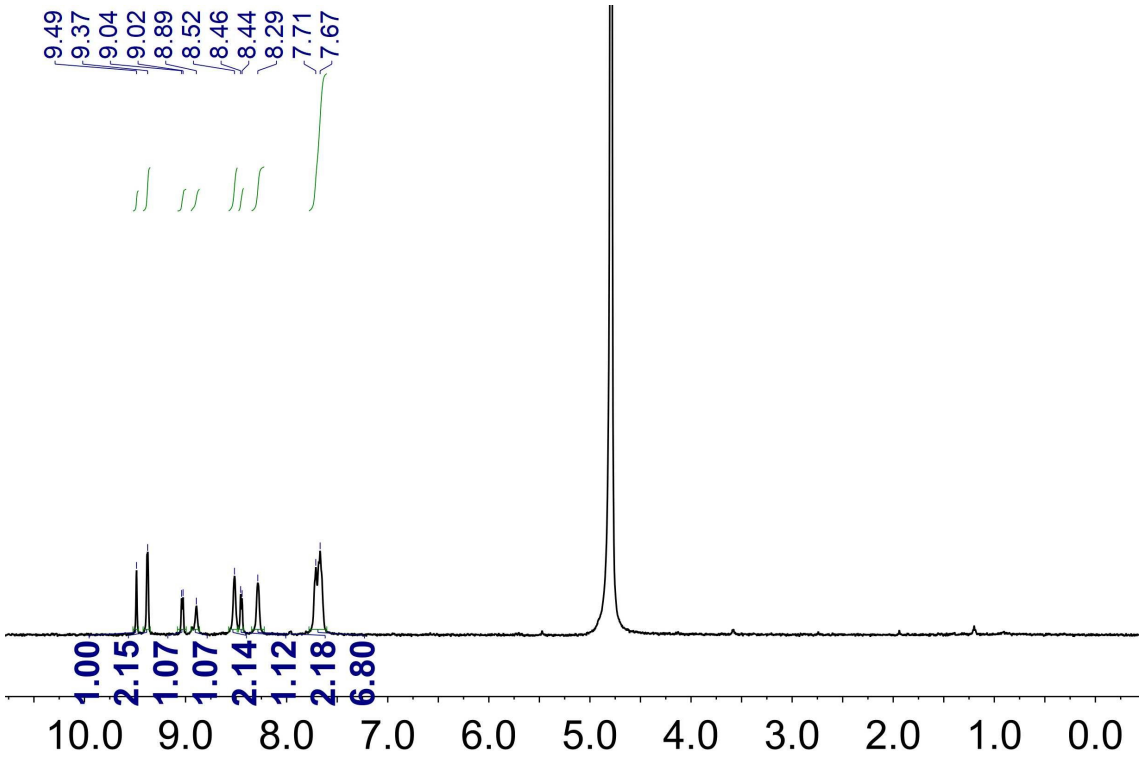


Figure S7 The ^{1}H NMR spectrum of compound **1-2** (400 MHz, D_2O, 298 k).

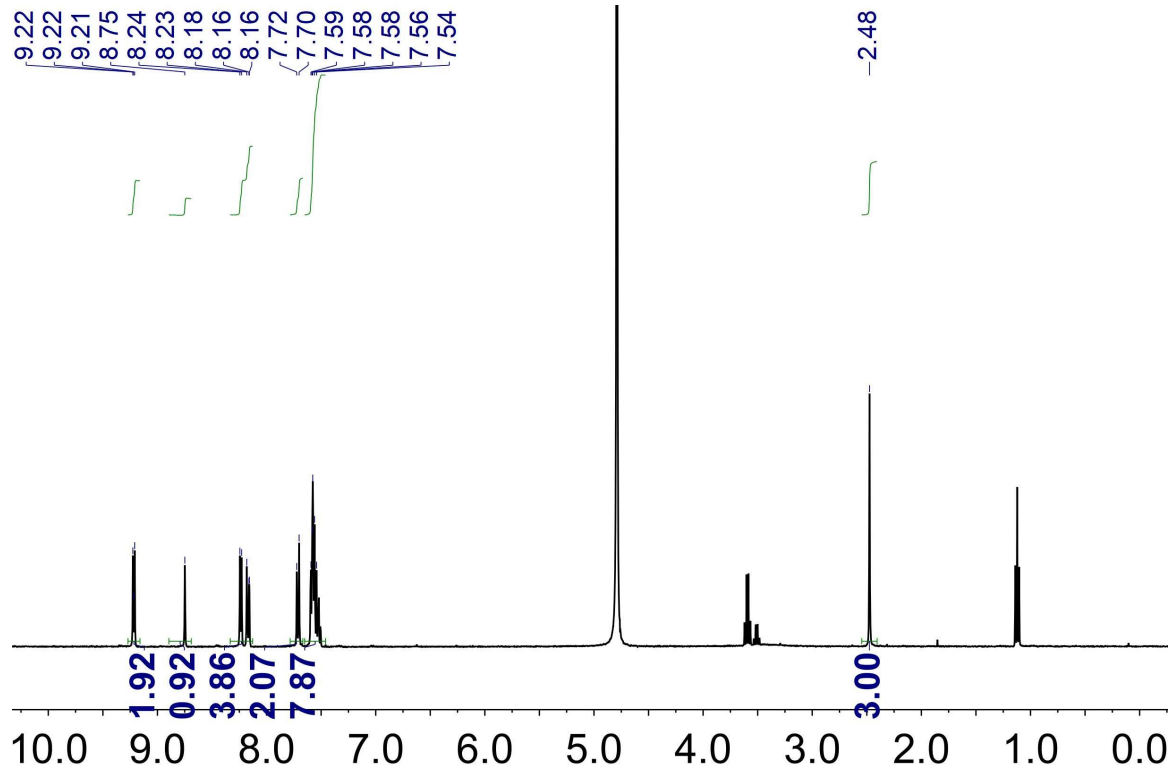


Figure S8 The ^{1}H NMR spectrum of compound **MPTA** (400 MHz, D_2O, 298 k).

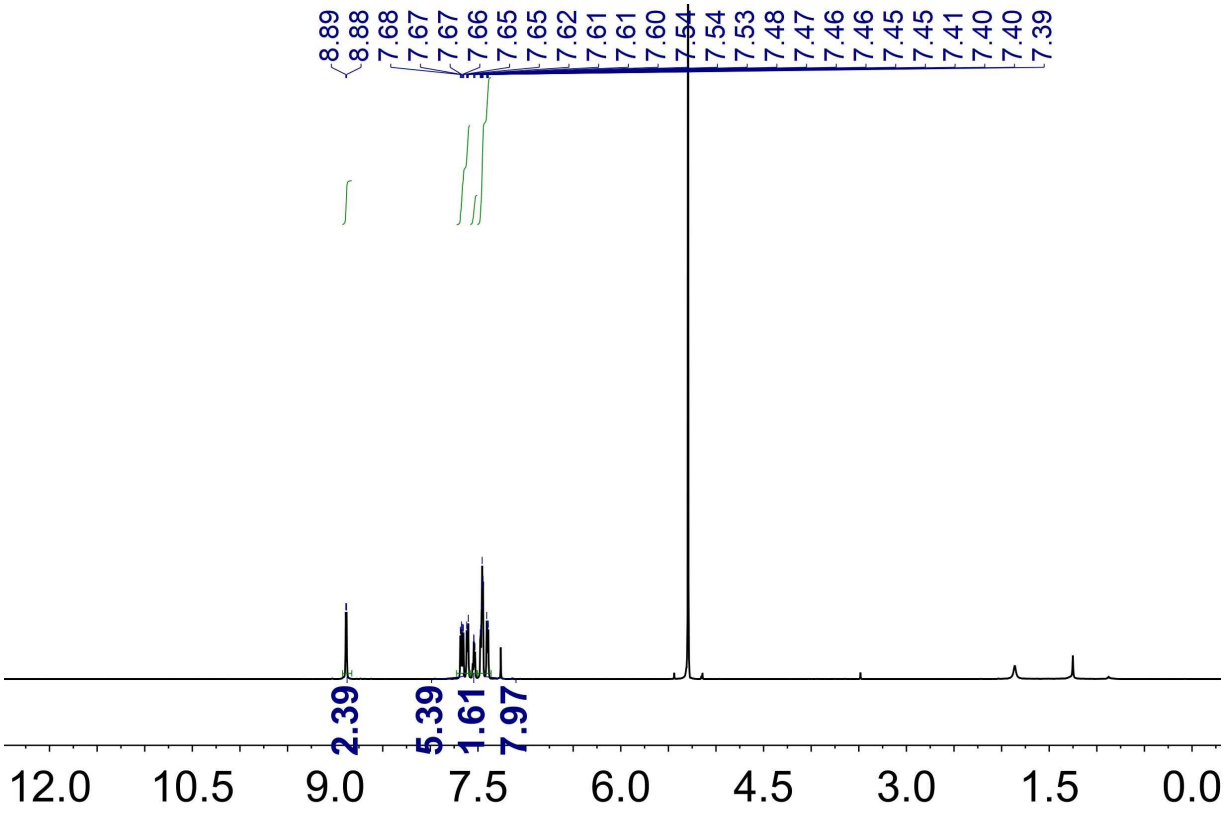


Figure S9 The ^{1}H NMR spectrum of compound **2-1** (400 MHz, $CDCl_3$, 298 k).

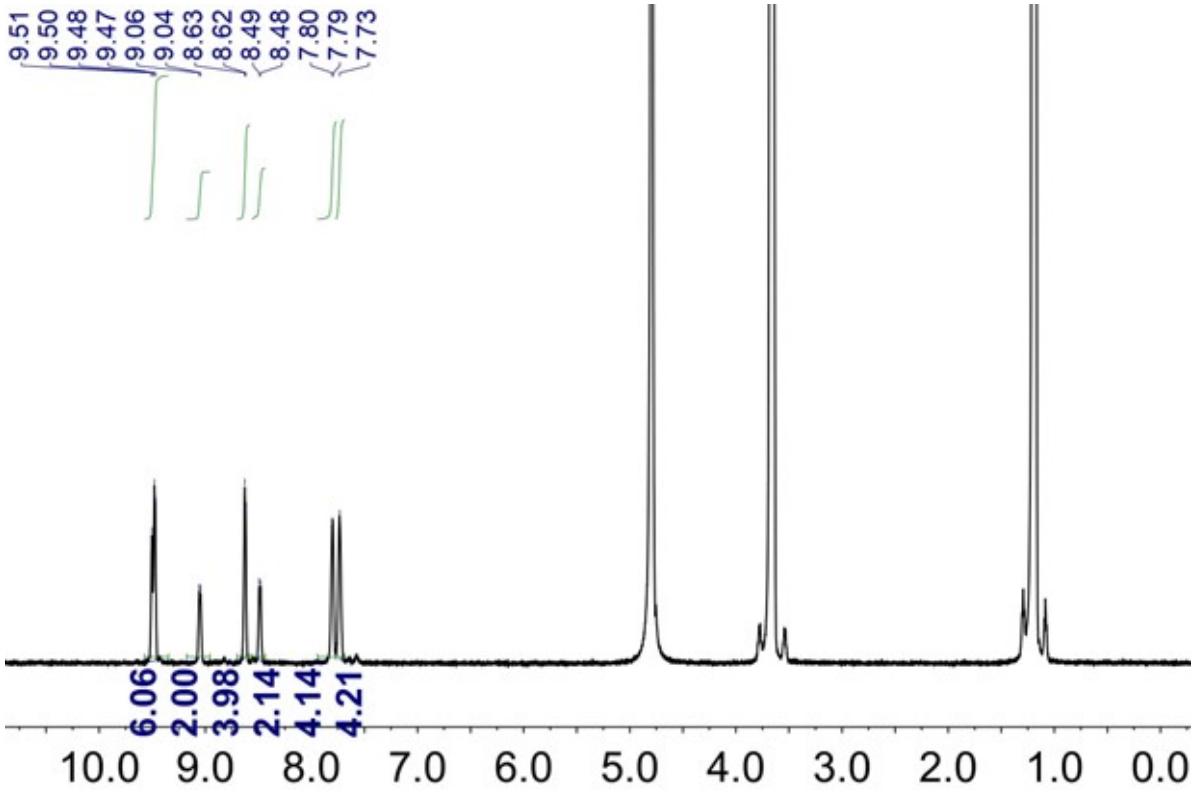


Figure S10 The ^{1}H NMR spectrum of compound **2-2** (400 MHz, D_2O, 298 k).

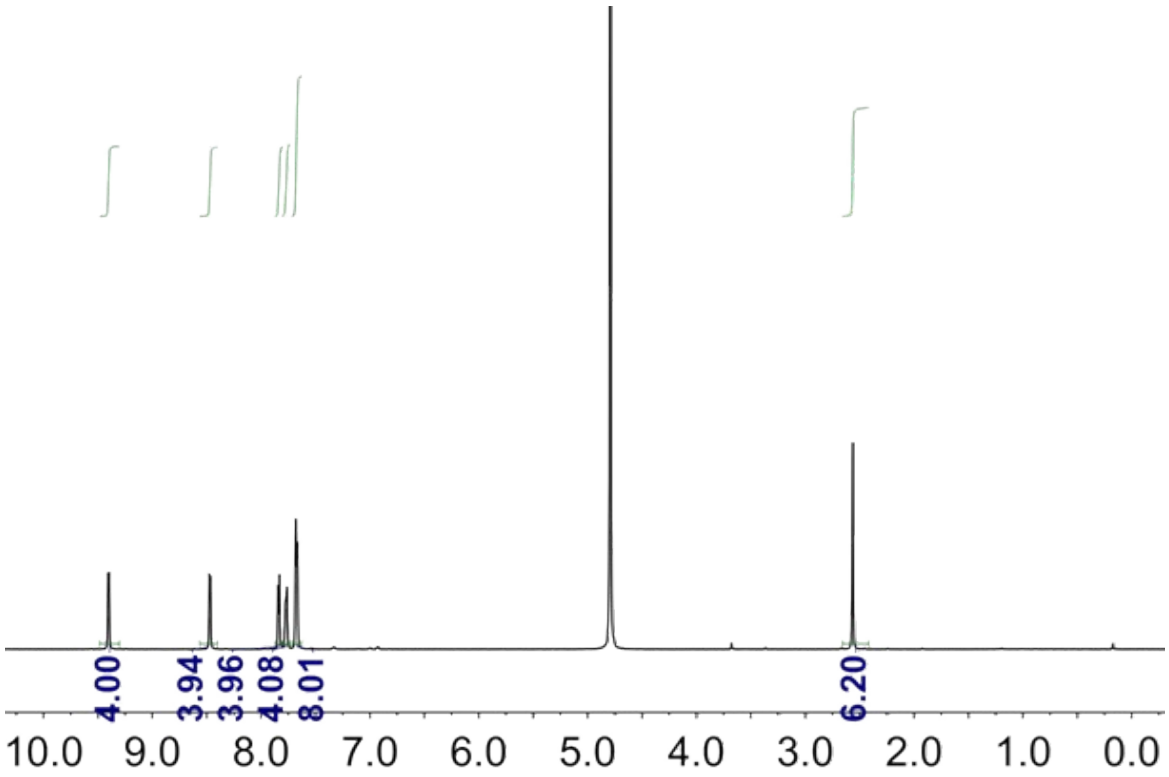


Figure S11 The ^{1}H NMR spectrum of compound **BPTA** (400 MHz, D_2O, 298 k).

DFT calculation

To verify the conformation of the two compounds **MTPA** and **BTPA**, DFT calculations were performed at the B3LYP-D3/6-31G(d) level of theory using the Gaussian 16 software.[5] No imaginary frequencies were found, which confirms achieving the energetic minima.

Table S1 Energies for the optimized structures at a B3LYP-D3/6-31G(d) level of theory (1 a. u. = 627.509608 kcal/mol).

Structure	Energy (a. u.)
MTPA	-1057.557190
BTPA	-1575.521219

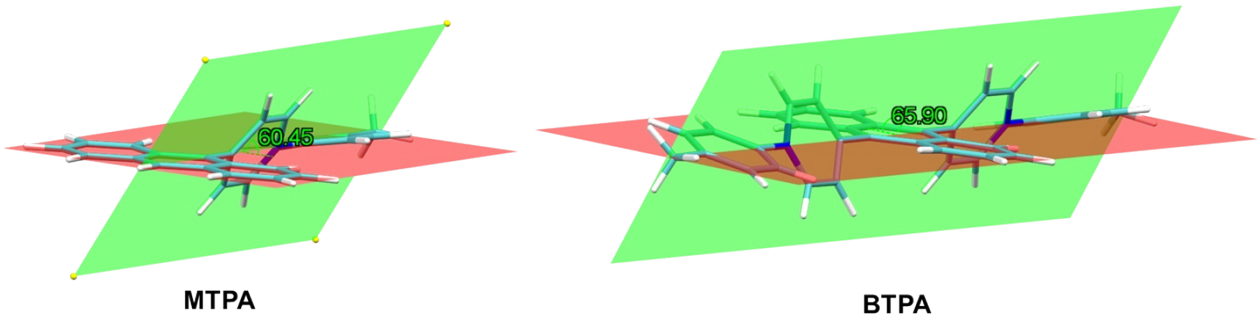


Figure S12 Optimized structures of **MTPA** (left) and **BTPA** (right).

Coordinates of B3LYP-D3/6-31G(d) optimized geometries for the two compounds (**MTPA** and **BTPA**).

MTPA

C	-4.09921108	1.22032823	0.03864973
C	-2.65536528	1.23266642	0.04776976
C	-1.95758929	-0.00019914	-0.00008838
C	-2.65505515	-1.23320313	-0.04846714
C	-4.09890966	-1.22118553	-0.04051526
C	-4.77751436	-0.00050403	-0.00121600
C	-4.81217939	2.45766563	0.08545072
C	-4.14688755	3.65195189	0.15494153
C	-2.72468916	3.66810847	0.19870643
C	-2.00416456	2.50206011	0.15381117
C	-2.00346960	-2.50244181	-0.15394516
C	-2.72369188	-3.66865332	-0.19943343
C	-4.14593271	-3.65281726	-0.15685384
C	-4.81155722	-2.45868472	-0.08790334
H	-5.86456426	-0.00062229	-0.00166291
C	-0.47918660	-0.00001139	0.00039359
C	0.25350571	0.64498321	-1.01125684
C	1.63120196	0.62529770	-0.99791054
N	2.30683808	0.00064172	0.00135271
C	1.63083313	-0.62448350	1.00006411
C	0.25312386	-0.64478776	1.01246746

C	3.75380285	0.00155070	0.00168225
C	4.43533807	1.20740821	-0.14814752
C	5.82838187	1.19668672	-0.14643683
C	6.54630188	0.00339440	0.00547115
C	5.82860715	-1.19196196	0.15955395
C	4.43729851	-1.20453369	0.15550458
C	8.05335027	-0.00447062	-0.01514352
H	-5.89802753	2.42477375	0.07115078
H	-4.69669552	4.58727121	0.19064475
H	-2.20381824	4.61746387	0.27850890
H	-0.92340453	2.54678802	0.21606355
H	-0.92264235	-2.54690575	-0.21528489
H	-2.20254233	-4.61789243	-0.27879375
H	-4.69549884	-4.58826128	-0.19301664
H	-5.89742442	-2.42603959	-0.07449868
H	-0.25249064	1.14090174	-1.83008347
H	2.23549030	1.07026735	-1.77629611
H	2.23463696	-1.06913958	1.77900712
H	-0.25319615	-1.14095821	1.83094315
H	3.89068826	2.14161287	-0.23550786
H	6.36367281	2.13522792	-0.25287371
H	6.36505688	-2.12911656	0.27447379
H	3.89305469	-2.13858604	0.24717615
H	8.45961298	0.99710938	0.15040462
H	8.45673531	-0.67377972	0.75156924
H	8.42543951	-0.35958976	-0.98428467

BTPA

C	0.72205008	-1.22800104	-0.00877375
C	-0.72207807	-1.22797230	0.00882034
C	-1.41434368	0.00219377	0.00042773
C	-0.72204868	1.23231247	-0.00836412
C	0.72209279	1.23228853	0.00828753
C	1.41435486	0.00215329	-0.00042689
C	1.40076684	-2.48664173	-0.05863321
C	0.70939310	-3.66835501	-0.03745556
C	-0.70954610	-3.66832001	0.03755330
C	-1.40086035	-2.48657244	0.05869954
C	-1.40082876	2.49092331	-0.05770327
C	-0.70943417	3.67263766	-0.03705502
C	0.70957320	3.67261333	0.03685255
C	1.40092134	2.49087363	0.05756873
C	2.89803053	0.00202380	-0.00077209
C	-2.89801509	0.00206611	0.00078178
C	-3.62429320	-0.49329617	-1.09291230

C	-5.00319351	-0.47538805	-1.07664283
N	-5.67661416	0.00043979	0.00179376
C	-5.00299243	0.47731631	1.07961813
C	-3.62407083	0.49690706	1.09484354
C	3.62407789	0.49689875	-1.09482275
C	5.00300201	0.47732576	-1.07958995
N	5.67661098	0.00044824	-0.00176549
C	5.00320759	-0.47539156	1.07667147
C	3.62430654	-0.49331183	1.09293890
C	7.12446380	-0.00132112	-0.00207109
C	-7.12445502	-0.00133765	0.00209840
C	7.80448011	-1.17457372	0.31944744
C	9.19677419	-1.16573612	0.31498704
C	9.91598513	-0.00652196	-0.00667125
C	9.19977336	1.15446944	-0.33091054
C	7.80796173	1.16907429	-0.32836301
C	-7.80448488	-1.17448247	-0.31975695
C	-9.19678827	-1.16563955	-0.31531358
C	-9.91600053	-0.00652842	0.00666187
C	-9.19977595	1.15437284	0.33124393
C	-7.80797575	1.16896982	0.32871575
C	11.42282121	-0.00007117	0.01841331
C	-11.42283449	0.00000507	-0.01842133
H	2.48205151	-2.50394705	-0.12158138
H	1.24644090	-4.61076074	-0.07506176
H	-1.24664143	-4.61069783	0.07517667
H	-2.48214972	-2.50381423	0.12162905
H	-2.48217375	2.50816984	-0.11979916
H	-1.24650679	4.61504563	-0.07424971
H	1.24668176	4.61500296	0.07399371
H	2.48226803	2.50807587	0.11966706
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H	-5.60828155	-0.80815001	-1.90861553
H	-5.60774983	0.80909747	1.91221701
H	-3.11559557	0.87734392	1.97198230
H	3.11559451	0.87734489	-1.97195243
H	5.60777217	0.80915261	-1.91216302
H	5.60831193	-0.80817100	1.90862719
H	3.11600536	-0.87321357	1.97040839
H	7.25860362	-2.08572361	0.54009962
H	9.73135164	-2.08004747	0.55368977
H	9.73703665	2.06450575	-0.58015652
H	7.26463423	2.08046462	-0.55428825
H	-7.25863680	-2.08559228	-0.54064051
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H	-9.73702908	2.06435008	0.58073525
H	-7.26466699	2.08031290	0.55487378
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H	11.79097284	0.33560092	0.99619993
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H	-11.79097760	0.33853154	-0.99522593

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