

Solid state photodimerization of *trans*-2-(4-pyridyl)-4-vinylbenzoic acid via salt formation and isomerisation of cyclobutane compounds in solution

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Supporting Information

Experimental Section

Trans-2-(4-pyridyl)-4-vinylbenzoic acid or HPVBA was synthesized by modifying the literature reported method.¹ HPVBA was allowed to react with the strong acids and amines to form molecular salts. The diffraction quality single crystals were obtained by slowly evaporating the alcoholic solutions. The yields of these crystallization processes vary in the range of 90 – 95 %. The single crystals or the powder samples were irradiated under UV light and their photoreactivity have been confirmed by ¹H-NMR spectroscopy. All the salts were characterized by NMR, elemental analysis and thermogravimetric analysis, UV-Vis and photoluminescence spectroscopy.

Elemental analysis was carried out at the Elemental Analysis Laboratory, CMMAC, the Department of Chemistry, National University of Singapore. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere with a heating rate of 5°C min⁻¹ on a SDT 2960 Thermal Analyzer. NMR spectra were recorded on a 300 MHz FT-NMR spectrometer with TMS as an internal reference. Photoluminescence spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-2450 spectrometer.

Intensity data for single crystalline compounds were collected at 100(2) K or 223(2) K on a Bruker APEX diffractometer that was attached with a CCD detector and graphite-monochromated Mo K α ($\alpha = 0.71073$ Å) radiation through a sealed tube (2.4 kW). The empirical absorption corrections were applied to the data by using the SADABS program.²

The structures were solved by using direct methods and refined on F^2 by full-matrix least-squares procedures with SHELXTL.³

(H₂PVBA)(CF₃CO₂) (1)

¹H NMR (300 MHz, *d*₆-DMSO, 298K): δ_{H} 8.78 (d, 2H, Py-H), 8.05 (d, 2H, Ar-H), 8.01 (d, 2H, Py-H), 7.91 (d, 1H, CH=CH), 7.84 (d, 2H, Ar-H), 7.58 (d, 1H, CH=CH). Analysis found (%): C 56.84, H 3.42, N 4.09; C₁₆H₁₂F₃NO₄ requires C 56.64, H 3.56, N 4.13. No solvent loss was observed in TGA experiment.

(H₂PVBA)ClO₄·MeOH (2)

¹H NMR (300 MHz, *d*₆-DMSO, 298K): δ_{H} 8.86 (d, 2H, Py-H), 8.21 (d, 2H, Ar-H), 8.06 – 8.0 (m, 3H, CH=CH and Py-H), 7.84 (d, 2H, Ar-H), 7.65 (d, 1H, CH=CH). Analysis found (%): C 51.95, H 3.84, N 4.08; C₁₄H₁₁ClNO₆ (excluding MeOH from formula unit) requires C 51.79, H 3.41, N 4.31.

After UV irradiation for 40 h, ¹H NMR (300 MHz, *d*₆-DMSO, 298K): δ 8.68 (d, 4H, Py-H), 7.91 (d, 4H, Ar-H), 7.80 (d, 4H, Py-H), 7.39 (d, 4H, Ar-H), 5.01 (m, 4H, CH-CH). ¹H-NMR (300 MHz, *d*₆-DMSO, 298K) of HT-4,4-BCBPCB (after neutralisation): δ_{H} 12.82 (s, 2H, CO₂H), 8.32 (d, 4H, Py-H), 7.78 (d, 4H, Ar-H), 7.35 (d, 4H, Ar-H), 7.21 (d, 4H, Py-H), 4.69 (m, 4H, CH-CH).

(H₂PVBA)₄(HSO₄)(SO₄)·H₂O (4)

¹H NMR (300 MHz, *d*₆-DMSO, 298K): δ_{H} 7.79 (d, 2H, Py-H), 8.07 (d, 2H, Ar-H), 8.01 (d, 2H, Ar-H), 7.94 (d, 1H, CH=CH), 7.79 (d, 2H, Py-H), 7.60 (d, 1H, CH=CH). Analysis found (%): C 54.97, H 4.60, N 4.47; C₅₆H₅₂N₄O₂₁S₃ requires C 55.44, H 4.32, N 4.62. The calculated and observed water losses in TGA experiment are 1.5 and 1.8%.

The representative peaks for photodimerization after UV irradiation for 50 h, ¹H NMR (300 MHz, *d*₆-DMSO, 298K): δ_{H} 8.56 (d, 4H, Py-H), 7.76 (d, 4H, Ar-H), 7.63 (d, 4H, Py-H), 7.39 (d, 4H, Ar-H), 4.91 (s, 4H, CH-CH).

(H₂PVBA)₃(HSO₄)₃(H₂SO₄)(H₂O)_{6.5} (5)

Analysis found (%): C 42.67, H 4.13, N 3.41; C₄₂H₅₄N₃O_{28.5}S₄ requires C 42.56, H 4.59, N 3.55. This composition is supported by the observed water loss in TGA experiment.

The observed water loss 9.7% is well agreement with the calculated value 9.8% for the proposed formula.

After irradiation under UV light 50 h, it was dissolved in water (monomer salt is weakly soluble in water) and then was dried. ^1H NMR (300 MHz, d_6 -DMSO, 298K): δ_{H} 8.55 (d, 4H, Py-H), 8.06 (d, 4H, Ar-H), 7.73 (d, 4H, Py-H), 7.35 (d, 4H, Ar-H), 4.93 (d, 2H, CH-CH), 4.83 (d, 2H, CH-CH). Two doublet peaks for cyclobutane protons indicate the formation of HH-photodimer. After neutralization, ^1H NMR (300 MHz, d_6 -DMSO, 298K): δ_{H} 12.78 (s, CO_2H), 8.33 (d, 4H, Py-H), 7.71 (d, 4H, Ar-H), 7.32 (d, 4H, Py-H), 7.23 (d, 4H, Ar-H), 4.68 (d, 4H, CH-CH).

(H₂PVBA)NO₃ (6)

^1H NMR (300 MHz, d_6 -DMSO, 298K): δ_{H} 8.86 (d, 2H, Py-H), 8.20 (d, 2H, Ar-H), 8.06 – 8.01 (m, 1H, CH=CH and 2H, Py-H), 7.86 (d, 2H, Ar-H), 7.66 (d, 1H, CH=CH). After UV irradiation for 30 h, ^1H -NMR (300 MHz, d_6 -DMSO, 298K): δ_{H} 8.70 (d, 4H, Py-H), 7.87 (d, 4H, Ar-H), 7.76 (d, 4H, py-H), 7.40 (d, 4H, Ar-H), 5.04 (m, 4-H, CH-CH). Analysis found (%): C 58.01, H 4.14, N 9.36; $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_5$ requires C 58.33, H 4.20, N 9.72. There was no solvent loss in TGA experiment.

PVBA-DABH salt (7)

^1H NMR (300 MHz, d_6 -DMSO, 298K): δ_{H} 8.54 (d, 2H, Py-H), 7.86 (d, 2H, Ar-H), 7.58 – 7.52 (m, 5H, Ar-H, Py-H, CH-CH), 7.25 (d, 1H, CH-CH), 2.62 and 1.42 (m, CH_2 , DAB). The representative peaks for HT-dimer after irradiation under UV light for 40 h, ^1H NMR (300 MHz, d_6 -DMSO, 298K): δ_{H} 8.33 – 8.28 (m, 8H, Py-H, Ar-H), 7.22 – 7.12 (m, 8H, Py-H, Ar-H), 4.60 (s, 4H, CH-CH).'

(HT-4,4-BPCCB)(4,4'-bpe)(MeOH)_{0.75}(H₂O)₂ (8)

4,4'-Bpe (18 mg, 0.1 mmol) and HT-BCBPCB (45 mg, 0.1 mmol) were dissolved in 4 mL methanol and 1 ml DMF. The resulting solution was kept for slow evaporation and diffraction quality block shaped single crystals were obtained after a few days. Yield 80%.

^1H NMR (300 MHz, d_6 -DMSO, 298K): δ_{H} = 12.82 (s, 2H, $-\text{CO}_2\text{H}$), 8.60 (d, 4H, Ar-H), 8.31 (d, 4H, Ar-H), 7.73 (d, 4H, Ar-H), 7.61 (d, 4H, Ar-H), 7.54 (s, 2H, CH=CH), 7.35 (d, 4H, Ar-H), 7.21 (d, 4H, Ar-H), 4.69 (s, 4H, CH-CH). Analysis found (%): C 70.87, H 5.13, N

8.17; $C_{40.75}H_{37}N_4O_{6.75}$ requires: C 70.65, H 5.67, N 8.09. In TGA experiment 7.5% solvent loss was observed, where the calculated value is 8.6%.

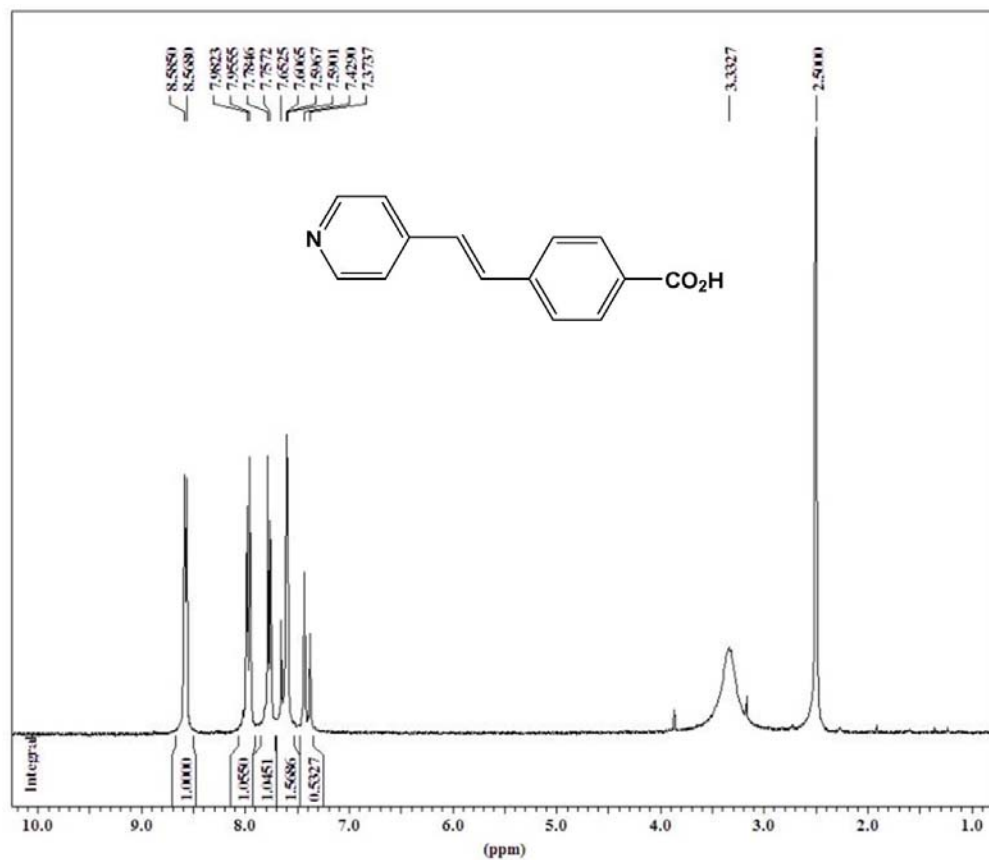


Figure S1: ^1H NMR spectrum of as synthesized HPVBA in d_6 -DMSO

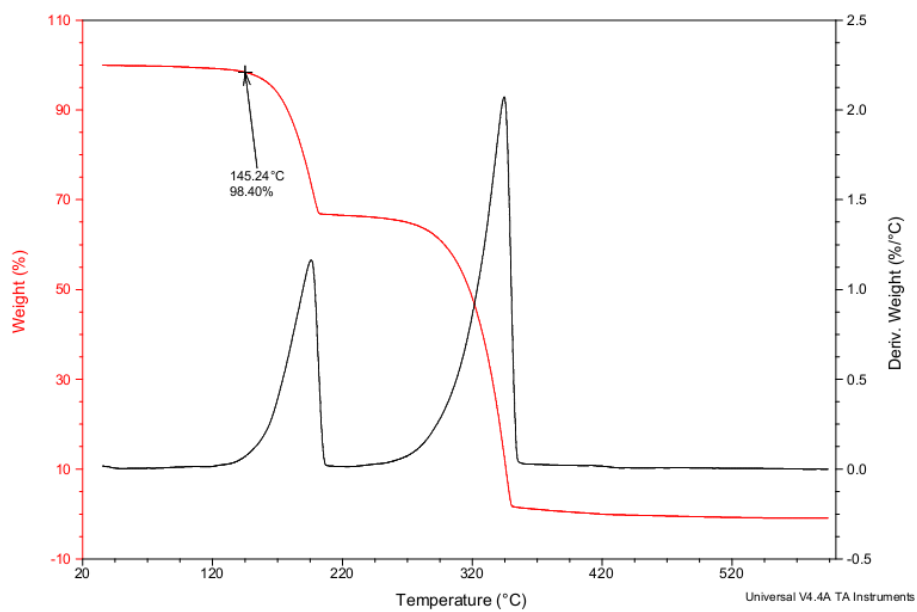


Figure S2: TGA plot of salt **1** shows no solvent loss.

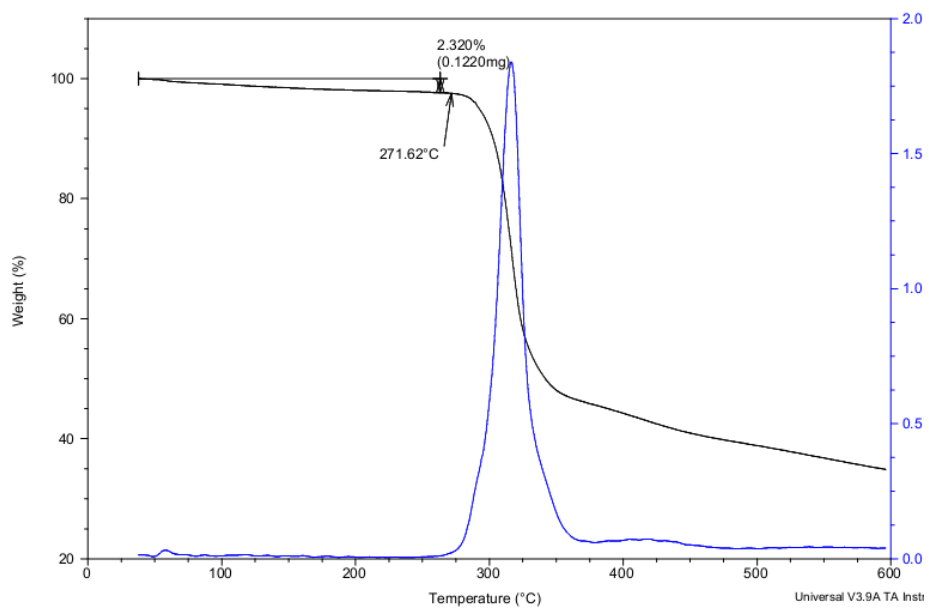


Figure S3: TGA plot for salt **2**

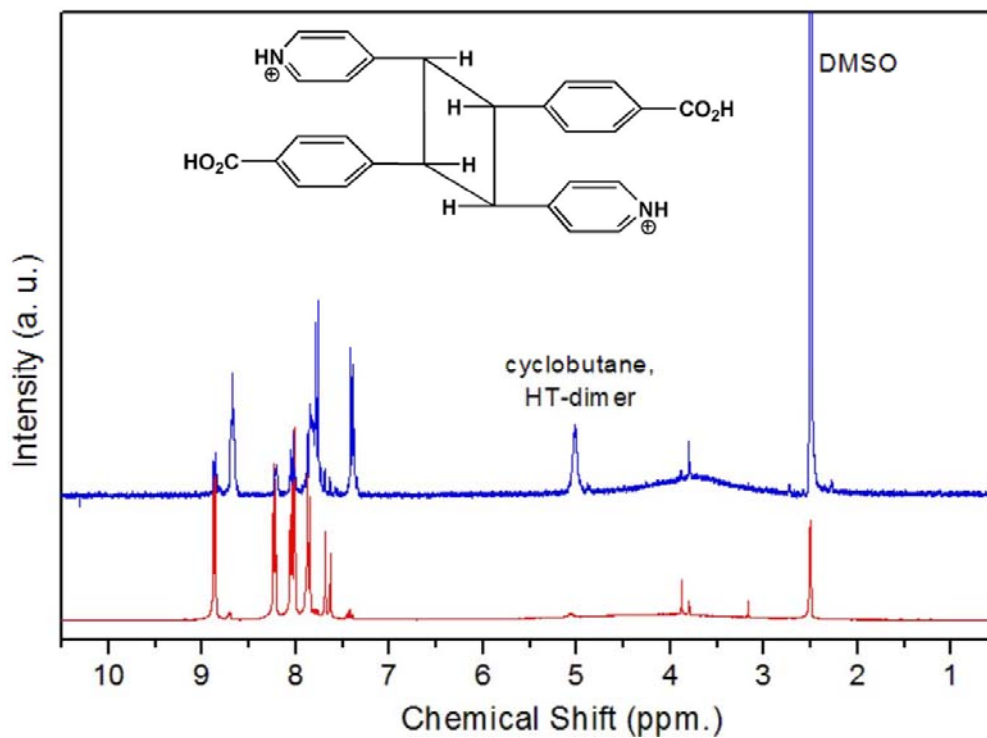


Figure S4: ¹H NMR spectra of salt (H₂PVBA)ClO₄ (**2**) in d₆-DMSO before and after photodimerization. It shows that incomplete conversion has taken place.

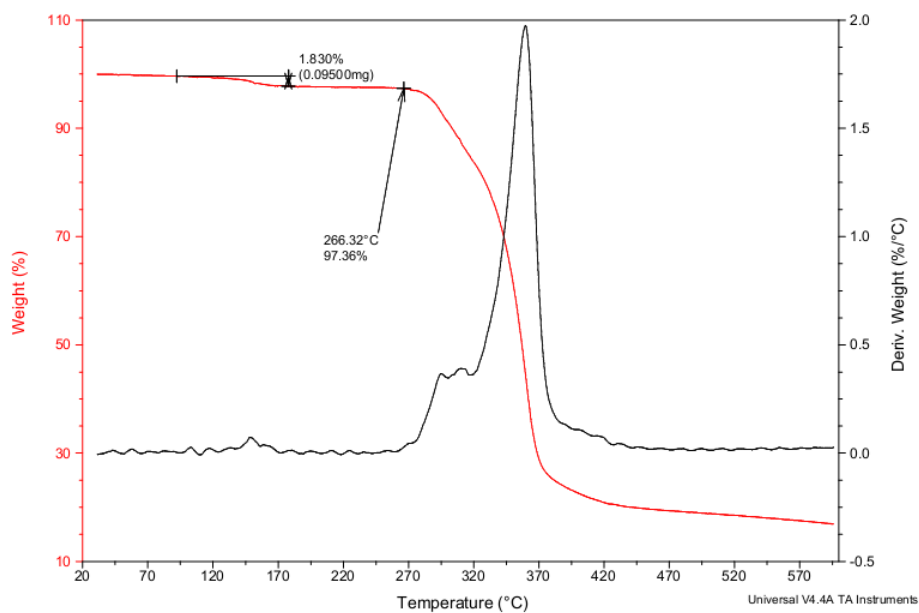


Figure S5: TGA plot for single crystals of salt **4**: calculated water loss 1.5% and observed 1.8%.

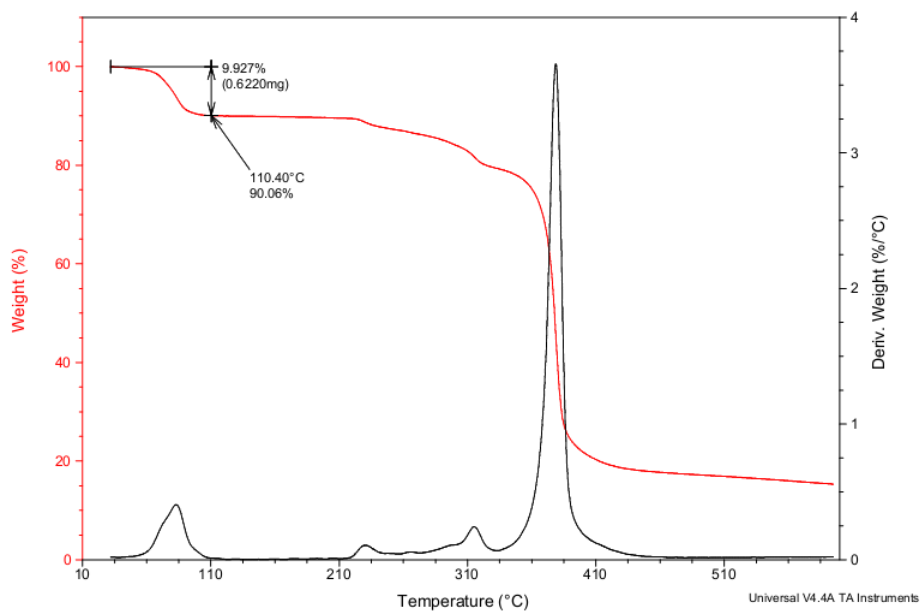


Figure S6: TGA plot for salt **5**: calculated water loss 9.8%, observed 9.9%.

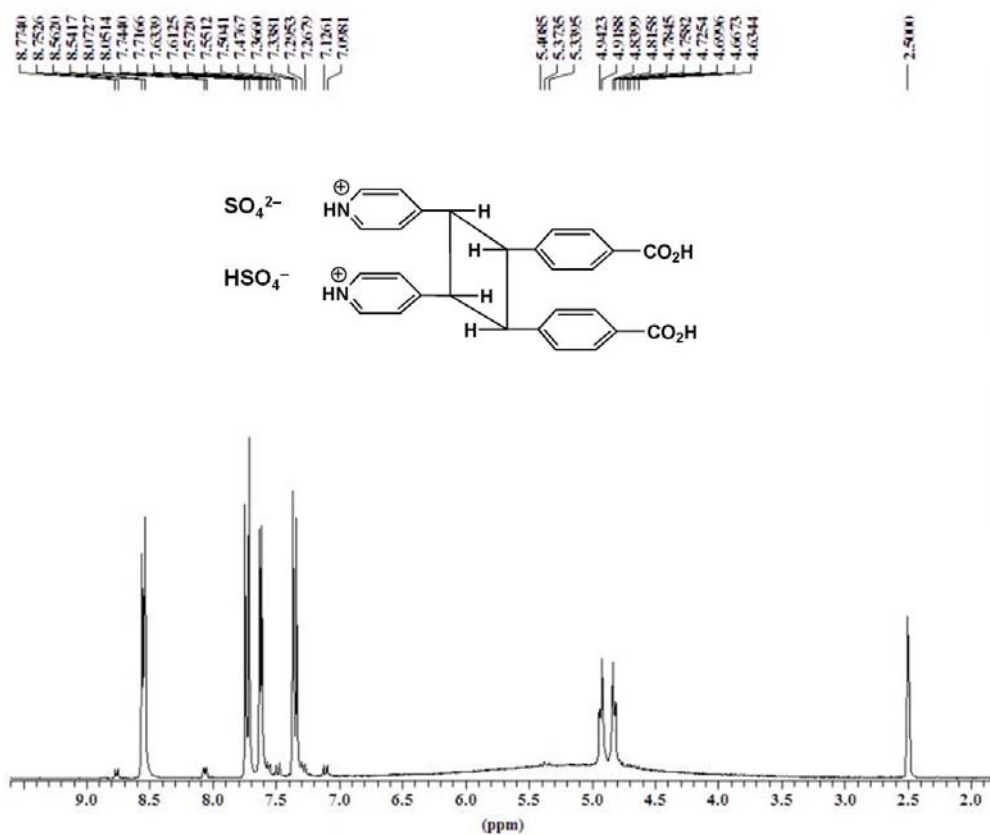


Figure S7: ¹H NMR spectrum (in *d*₆-DMSO) of salt **5** after irradiation under UV light. It shows that photodimerization has taken place in HH-fashion.

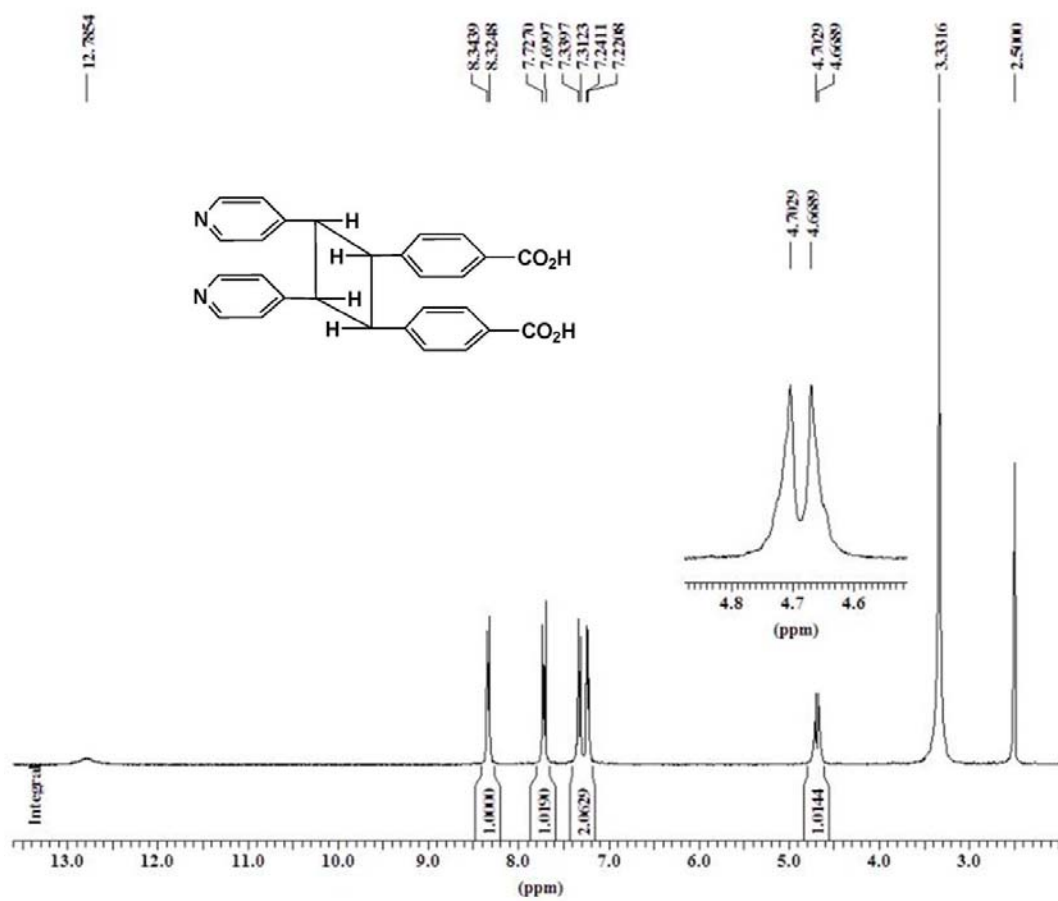


Figure S8: ¹H NMR spectrum for neutralised HH-dimer, *rctt*-HH-BPBCCB in *d*₆-DMSO

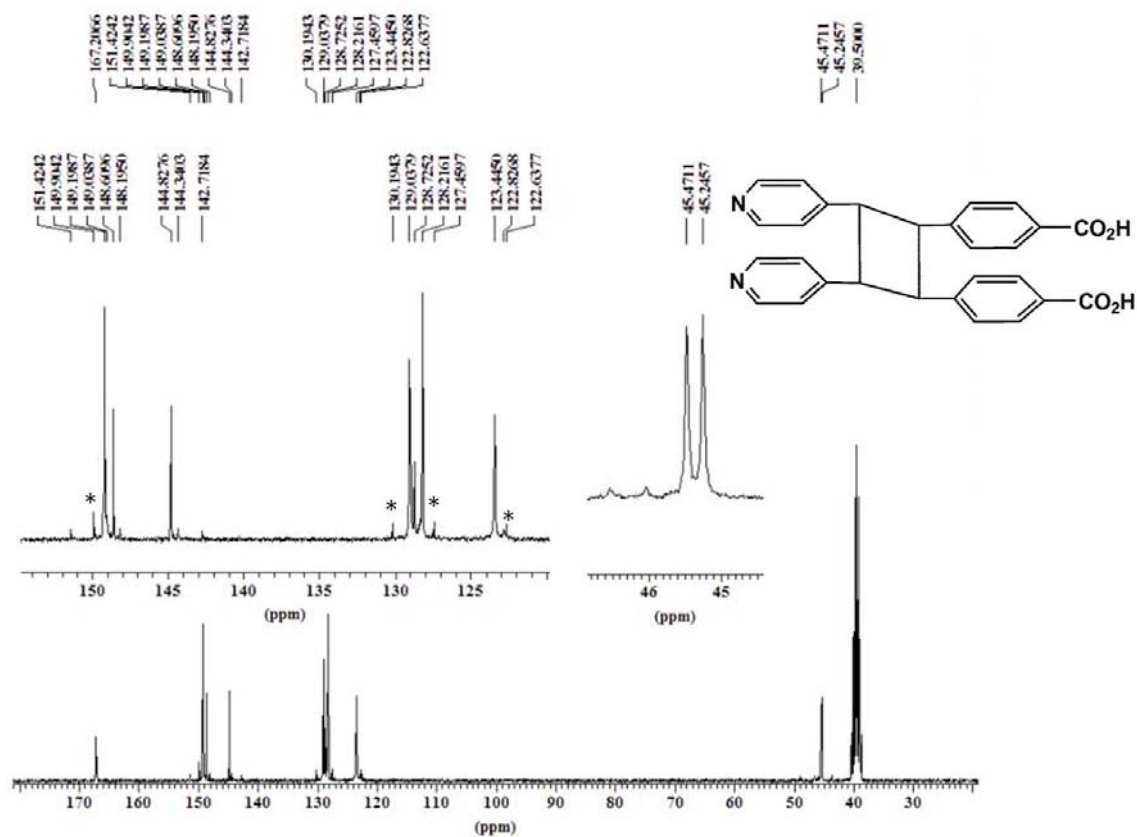


Figure S9: ^{13}C NMR spectrum for neutralised HH-dimer, HH-BPCCB in d_6 -DMSO. The peaks marked as asterisk, are due to the presence of a small amount of HPVBA monomer.

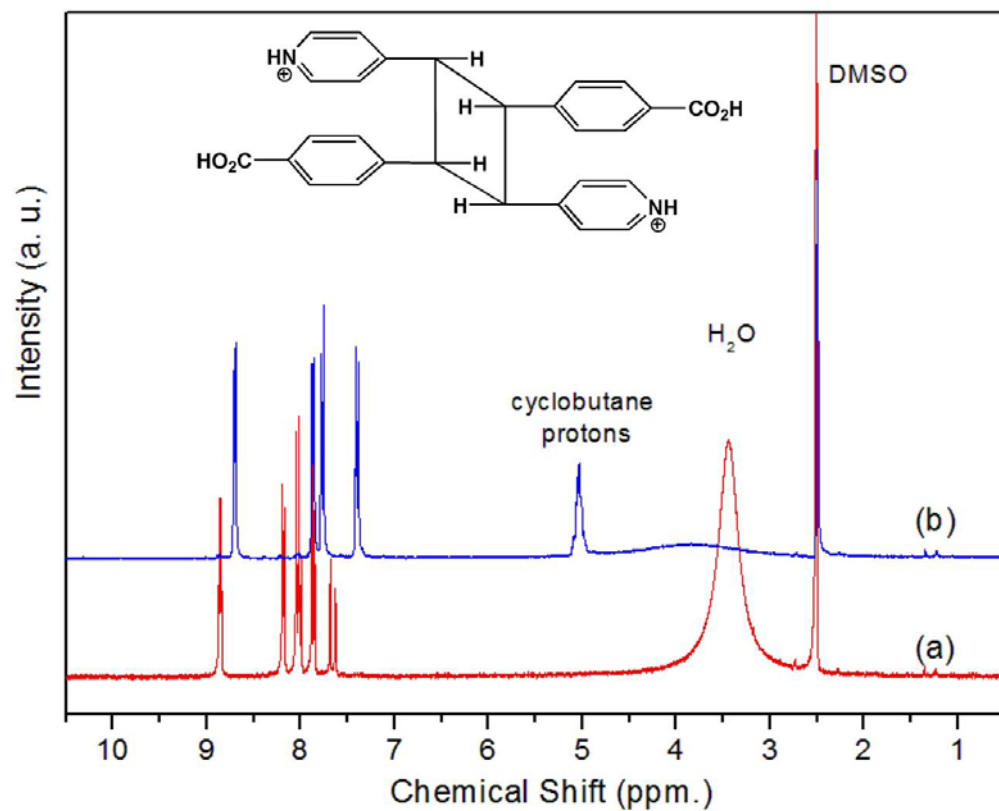


Figure S10: ^1H NMR spectra of salt $(\text{H}_2\text{PVBA})\text{NO}_3$ (**6**) in d_6 -DMSO before and after photodimerization. It shows 100 % conversion has taken place.

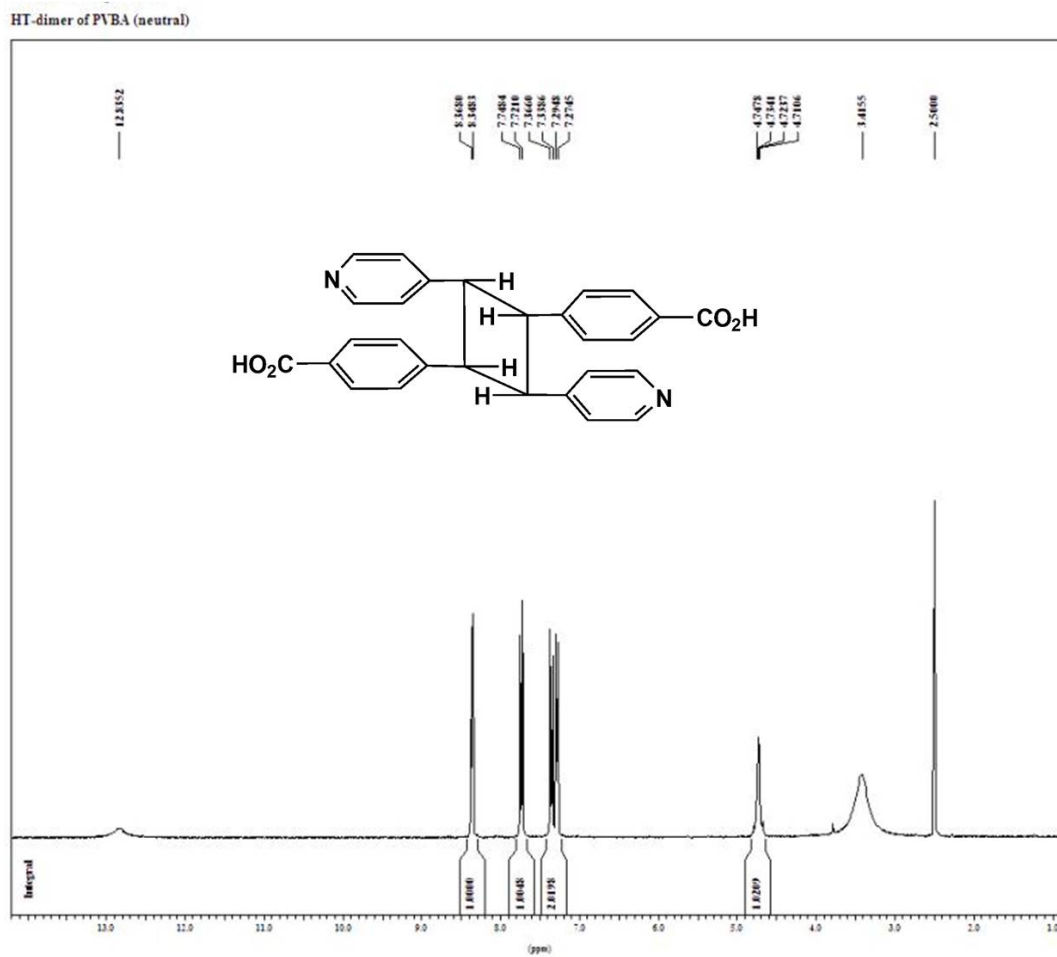


Figure S11: ¹H NMR spectrum for neutralised HT-dimer, *rctt*-HT-BPBCCB in *d*₆-DMSO.

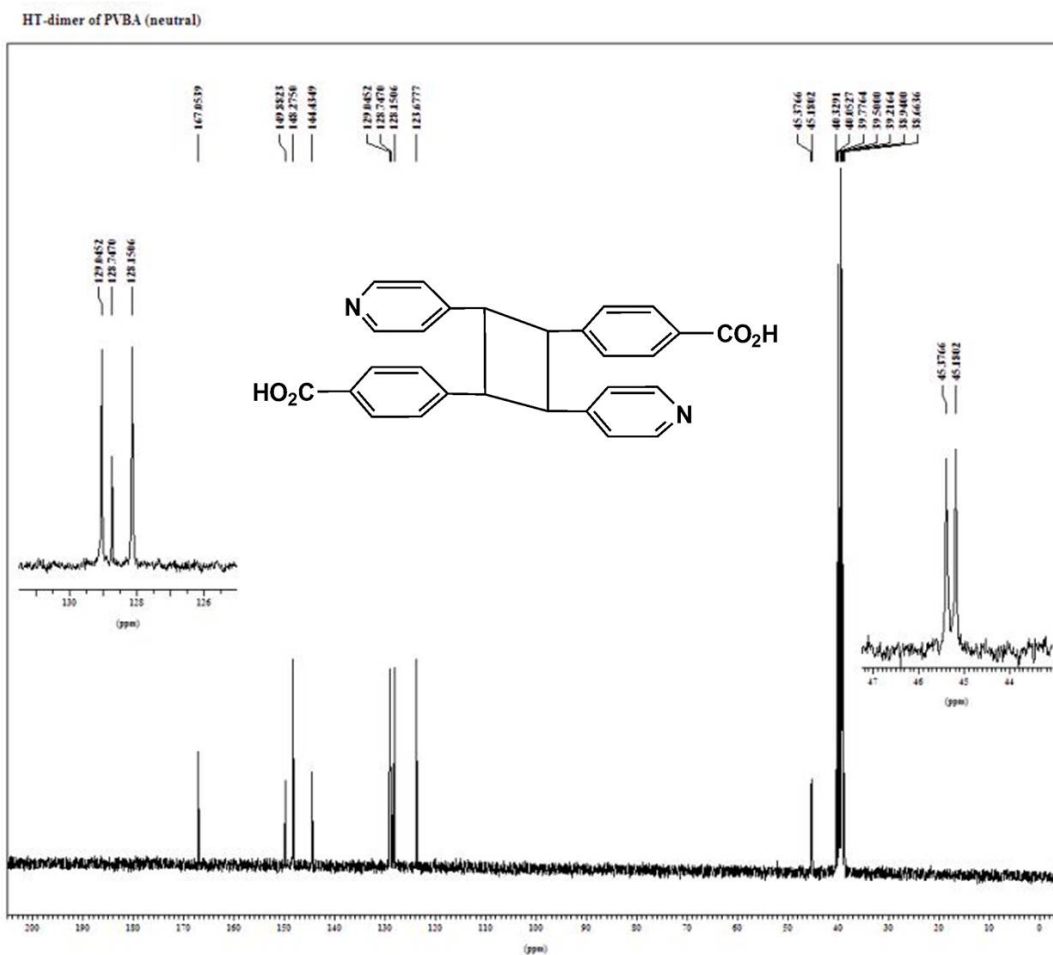


Figure S12: ¹³C NMR spectrum for neutralised HT-dimer, *rctt*-HT-BPCCB in *d*₆-DMSO.

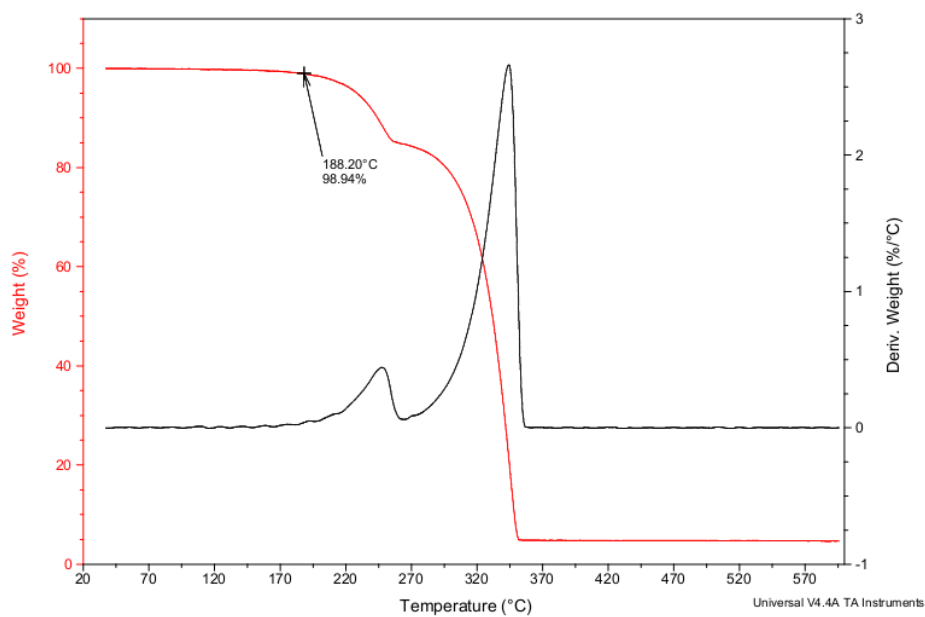


Figure S13: TGA plot for salt **6** shows no solvent loss.

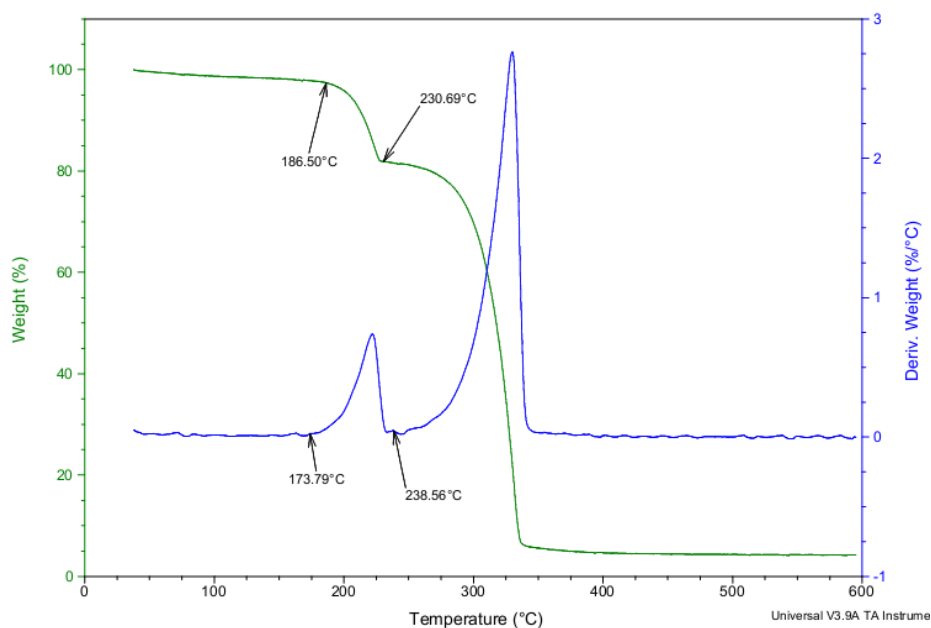


Figure S14: TGA plot for salt 7.

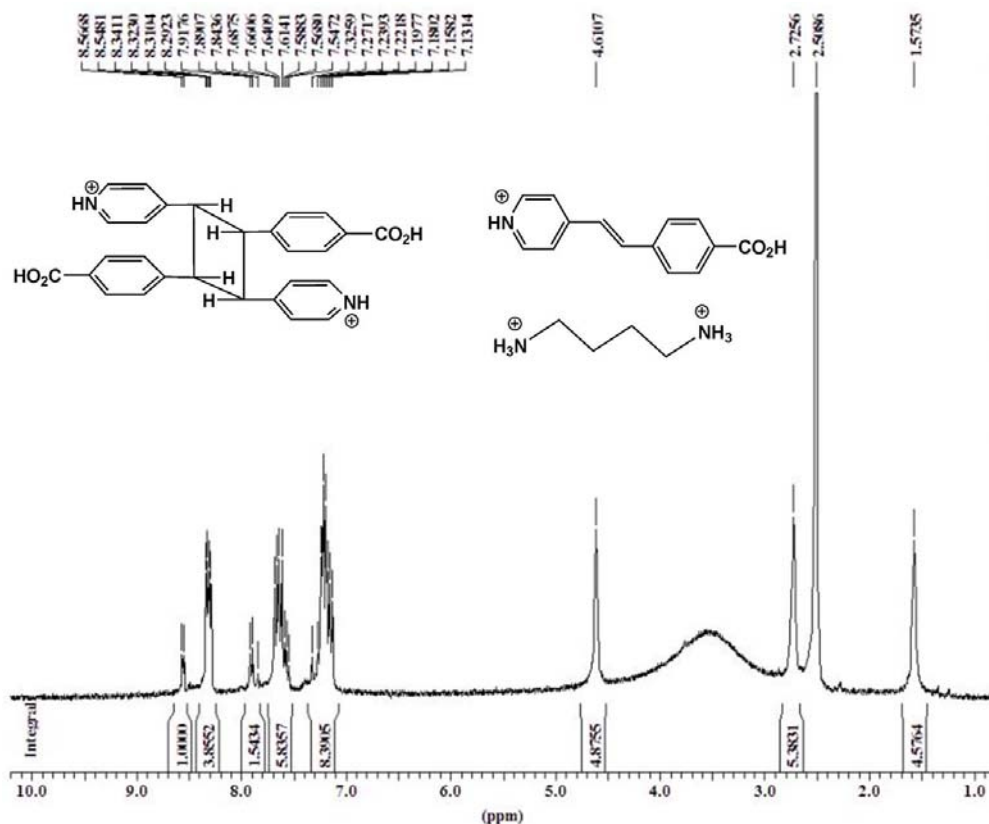


Figure S15: ¹H NMR spectra of salt PVBA-DABH (7) in *d*₆-DMSO after photodimerization.
It shows that ~ 80 % conversion has taken place.

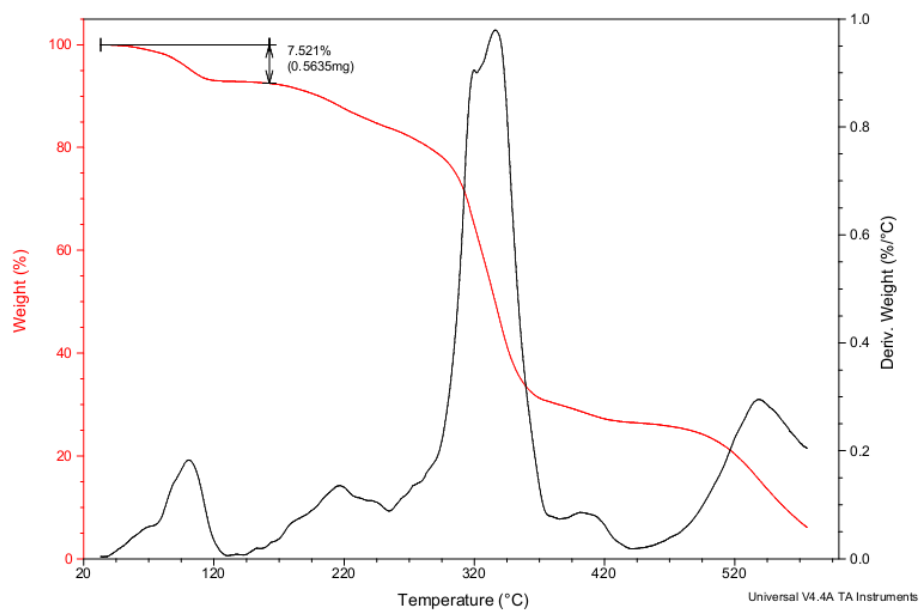


Figure S16: TGA plot for co-crystal **8**: calculated solvent loss 8.6%, observed 7.5%.

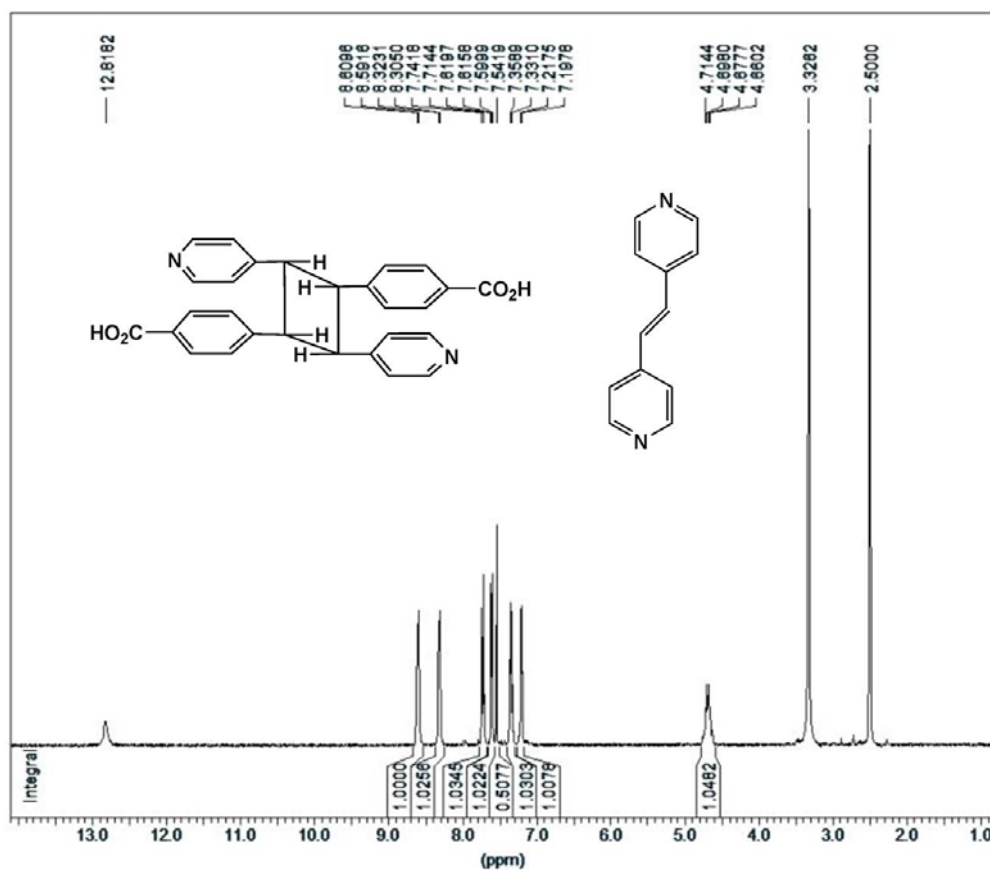


Figure S17: ¹H NMR spectrum (in *d*₆-DMSO) of co-crystal **8** shows the presence of both HT-BPCCB and 4,4'-bpe

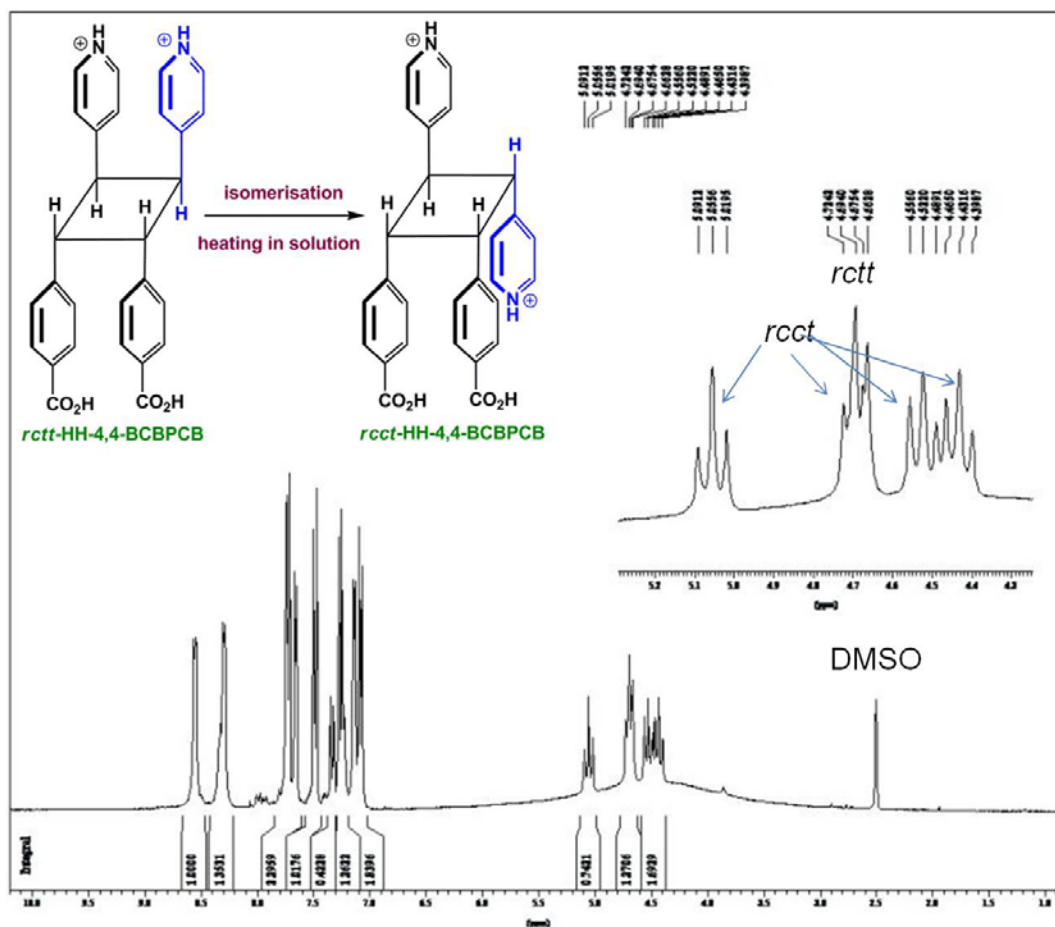


Figure S18: ¹H NMR spectrum (in *d*₆-DMSO) shows isomerisation of *rctt*-HH isomer to *rcct*-HH isomer. The degeneracy of cyclobutane protons is lifted due to symmetry-loss in isomerisation. The presence of four triplet peaks for *rcct*-HH isomer is consistent with our previous results.⁴ The presence cyclobutane peak or *rctt*-isomer indicates that the isomerisation is not quantitative.

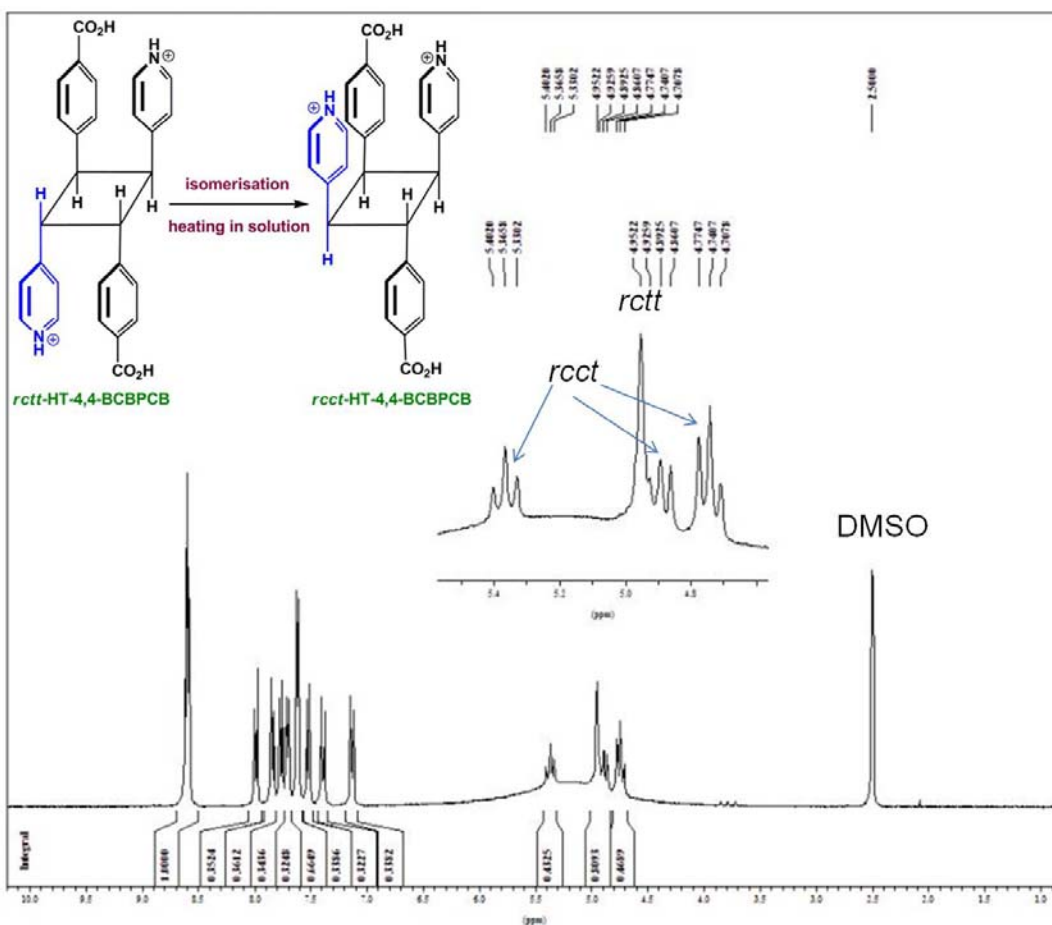


Figure S19: ¹H NMR spectrum (in *d*₆-DMSO) shows isomerisation of *rctt*-HT isomer to *rcct*-HT isomer. The degeneracy of cyclobutane protons is lifted due to symmetry-loss in isomerisation. The presence of three triplet peaks (1:1:2) for *rcct*-HT isomer is consistent with our previous results.⁴ The presence of cyclobutane peak or *rctt*-isomer indicates that this isomerisation is also not quantitative. This spectrum was obtained from heating trifluoroacetate salt of *rctt*-HT isomer as nitrate salt was found to decompose after heating.

UV-Vis and Photoluminescence Studies

All the salts were found to be emissive under UV light when irradiated for photodimerization reaction. Therefore, both the absorption and emission properties of all the salts were studied as solution in MeOH. In the UV-Vis spectra, it can be observed that the salts of the pyridyl-N protonated HPVBA (1 – 6) also show similar absorption behaviour having maximum absorption (λ_{\max}) at around 330 nm; whereas the λ_{\max} of salt where carboxyl-H is

deprotonated (**7**) shows considerable blue-shift (315 nm). After the photoreaction was completed under UV light, the absorption intensities dropped as no absorption peak could be observed above 280 nm. This observation of changing absorption properties upon UV irradiation, also support that photodimerization reaction proceeded.

The emission spectra were recorded with these samples excited at $\lambda = 333$ nm. Same excitation wavelength was used for all the samples for comparison. All the salts where the pyridyl-Ns are protonated, before and after photodimerization, showed weak emission (λ_{max}) at the range of 400 – 410 nm and salt **7**, where the carboxyl-H is deprotonated, emitted at 363 nm.

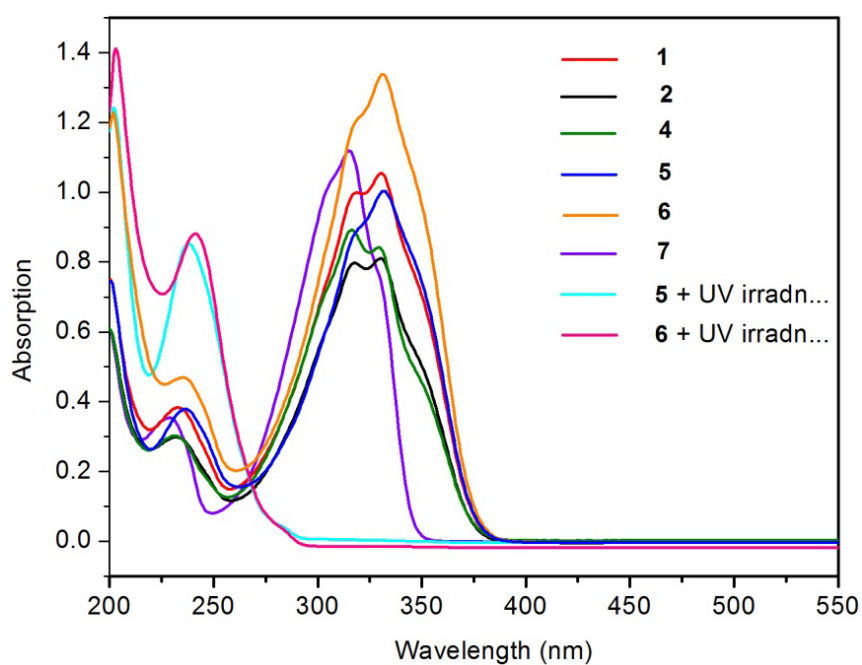


Figure S20: UV-Vis spectra of the salts of HPVBA, before and after photodimerization

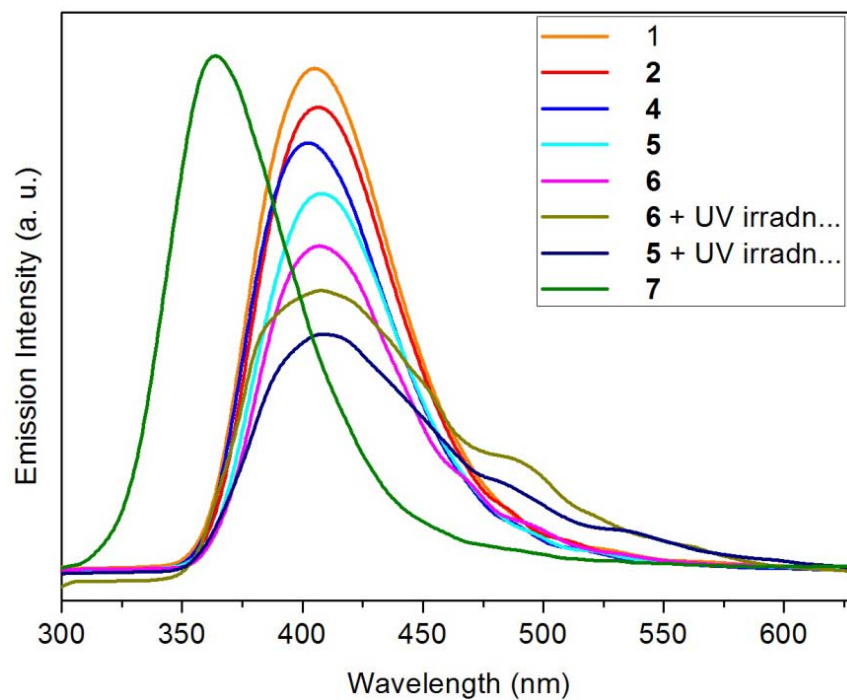


Figure S21: Photoluminescence spectra of the salts of HPVBA salts, before and after photodimerization

Crystallographic Data

Table 1: Crystallographic data for compounds **1**, **2**, **4** and **8**

Compounds	1	2	4	8
Formula	C ₁₆ H ₁₂ F ₃ NO ₄	C ₁₅ H ₁₆ ClNO ₇	C ₅₆ H ₅₂ N ₄ O ₂₁ S ₃	C _{40.75} H ₃₉ N ₄ O _{6.75}
<i>M</i>	339.27	357.74	1213.20	692.76
T (K)	100(2)	223(2)	223(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.2580(9)	8.6037(11)	11.1151(9)	10.1643(11)
<i>b</i> (Å)	8.4271(10)	9.5432(12)	11.8964(9)	10.1819(10)
<i>c</i> (Å)	12.6094(15)	10.2702(13)	22.1546(18)	34.305(4)
α (°)	77.860(2)	93.248(2)	91.414(2)	90
β (°)	75.529(2)	101.615(2)	98.911(2)	95.067(3)
γ (°)	72.829(3)	107.129(2)	110.246(2)	90
Volume (Å ³)	705.67(15)	783.27(17)	2705.6(4)	3536.4(6)
<i>Z</i>	2	2	2	4
<i>D</i> _{calcd} (g/cm ³)	1.597	1.517	1.489	1.301
μ (mm ⁻¹)	0.140	0.283	0.224	0.089
Reflns col.	9191	10107	35723	20322
Ind. Reflns.	3233	3589	12429	6205
<i>R</i> _{int}	0.0299	0.0357	0.0613	0.0839
Goof on F ²	1.091	1.221	1.035	1.072
Final <i>R</i> [<i>I</i> >2 σ] ^a	0.0578 / 0.1395	0.0784 /	0.0652 / 0.1352	0.0861 / 0.2053
<i>R</i> ₁ / w <i>R</i> ₂		0.2203		

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

Tables for Hydrogen Bonding Parameters

Table 2: The hydrogen bonding parameters for **1**

D-H...A	D(D-H) (Å)	D(H...A) (Å)	D(D...A) (Å)	<(DHA) (°)	Symmetry Operator
O(1)-H(1O)...O(4)	0.84	1.79	2.633(2)	175(3)	x, y, z-1
N(1)-H(1N)...O(3)	0.87	1.86	2.701(2)	163(3)	-x, -y+1, -z+1
C(10)-H(10)...O(1)	0.95	2.39	3.245(3)	148.4	-1+x, y, 1+z
C(14)-H(14)...O(2)	0.95	2.28	3.000(3)	131.5	x, -1+y, 1+z
C(13)-H(13)...F(1)	0.95	2.42	3.307(3)	154.9	x, -1+y, z
C(14)-H(14)...O(4)	0.95	2.57	3.339(3)	138.4	x, -1+y, z

Table 3: The hydrogen bonding parameters for **2**

D-H...A	D(D-H) (Å)	D(H...A) (Å)	D(D...A) (Å)	<(DHA) (°)	Symmetry Operator
N(1)-H(1A)...O(3)	0.87	2.16	2.935(7)	148.7	x, y-1, z
N(1A)-H(1AB)...Cl(1)	0.87	2.88	3.70(2)	158.6	x, y-1, z
O(1)-H(1)...O(1S)	0.83	1.75	2.574(4)	171.9	-x+1, -y+2, -z+1
O(1S)-H(1S)...O(2)	0.80	1.98	2.771(4)	173(5)	x+1, y, z-1

Table 4: The hydrogen bonding parameters for **4**

D-H...A	D(D-H) (Å)	D(H...A) (Å)	D(D...A) (Å)	<(DHA) (°)	Symmetry Operator
O1W-H1WB...O18	0.84	1.87	2.715(3)	173(4)	-x+1, -y+1, -z+1
O1W-H1WA...O12	0.85	1.95	2.783(3)	167(3)	x-1, y-1, z
O14-H14O...O20	0.87	1.69	2.524(3)	159(4)	
O9-H9O...O18	0.94	1.57	2.507(3)	176(4)	x, y, z+1
N4-H4N...O15	0.90	1.81	2.705(3)	175(3)	-x+1, -y+1, -z
N3-H3N...O19	0.90	1.75	2.658(3)	176(3)	-x+1, -y+1, -z
N2-H2N...O1W	0.91	1.72	2.631(3)	175(3)	x, y+1, z
N1-H1N...O11	0.90	1.81	2.709(3)	179(3)	-x+2, -y+1, -z+1
O7-H7...O2	0.83	1.81	2.642(3)	175.6	-x+1, -y+2, -z+1
O6-H6O...O5	1.26	1.35	2.613(3)	176(5)	-x, -y+2, -z+1
O3-H3...O16	0.83	1.82	2.595(3)	155.4	
O1-H1...O8	0.83	1.82	2.647(3)	176.4	-x+1, -y+2, -z+1
C11-H11...O3	0.94	2.57	3.448(4)	154.2	1+x, y, z
C12-H12...O15	0.94	2.42	3.279(4)	151.1	1+x, y, z
C13-H13...O17	0.94	2.39	3.083(4)	130.6	
C14-H14...O13	0.94	2.54	3.365(4)	146.6	
C18-H18...O16	0.94	2.40	3.325(4)	166.5	1-x, 1-y, 1-z
C26-H26...O10	0.94	2.30	3.161(4)	150.9	-1+x, y, z
C27-H27...O20	0.94	2.30	3.204(4)	160.8	1-x, 2-y, 1-z
C28-H28...O4	0.94	2.53	3.401(4)	153.8	1-x, 2-y, 1-z
C40-H40...O19	0.94	2.42	3.308(4)	157.9	
C40-H40...O20	0.94	2.59	3.345(4)	137.5	
C53-H53...O1W	0.94	2.38	3.296(4)	164.7	1-x, 1-y, 1-z
C54-H54...O11	0.94	2.31	3.205(4)	159.8	x, y, -1+z
C56-H56...O10	0.94	2.28	3.192(4)	162.8	-1+x, y, -1+z

Table 5: The hydrogen bonding parameters for **8**

D-H...A	D(D-H) (Å)	D(H...A) (Å)	D(D...A) (Å)	<(DHA) (°)	Symmetry Operator
O1-H1...N4	0.84	1.79	2.625(5)	177.1	-x+1/2, y+1/2, -z+1/2
O3-H3...N3	0.84	1.73	2.569(4)	174.6	x+1, y, z
O1W-H1WB...O2W	0.85	2.36	2.794(8)	112(5)	x+1, y, z
O1S-H1S...N2	0.84	2.09	2.764(8)	137.1	-x+3/2, y+1/2, -z+1/2
O1S-H1S...O4	0.84	2.48	2.945(8)	115.6	x-1, y, z

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