Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Croconic acid derived narrow band gap conjugated microporous polymer

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Materials:

All the reagents and solvents used in synthesizing model compounds and polymers were either synthesized or purchased commercially with >99% purity. Chemicals were used as received without any further purification unless noted. All solvents were of at least AR grade and dried if necessary. 4,5-dihydroxycyclopent-4-ene-1,2,3-trione (Croconic Acid) and 3,4-dihydroxycyclobut-3-ene-1,2-dione (Squaric Acid) were purchased from TCI. Chemicals (India) Pvt. Ltd. N^1,N^1-bis(4-aminophenyl)benzene-1,4-diamine (TPA-NH_2) was synthesized according to a previously published procedure[1] .

Material Characterizations:

The solution states ^{1}H, and ^{13}C NMR were recorded on Jeol JNM-ECZ400R/S1, and solid-state CP/MAS NMR was performed with the same instrument with a spinning frequency of 12 kHz, 3ms contact time and a relaxation delay of 10s. FT-IR (Fourier transform infrared spectra) analysis was recorded on Nicolet Impact-400 FT-IR spectrometer. Cary 3000 UV-Vis-NIR spectrophotometer was employed to identify the optical properties of the synthesized model molecules and polymers. Carl Zeiss Gemini 300FESEM was used to study the surface morphologies of the different layers present in the polymer. For nitrogen adsorption isotherm was obtained with Quanta Chrome Nova 2200e Surface Area & Pore Size Analyzer. Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C min^{-1} up to 800 °C using TGA-4000. Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS) System was used to study the elemental composition of the materials. Powder XRD was performed on an Empyrean 3rd Gen instrument. Density functional theory calculations of model molecules and CMPs were carried out using PBEPBE/6-31G(d) using Gaussian 16.

Iodine doping and Conductivity measurements:

The iodine doping was performed by exposing iodine vapours to ~15 mg of CMPs powder loaded in an open small glass vial (2 ml) which was then place inside a larger vial (10 ml) containing solid iodine (3 g). The larger vial was sealed and kept in an oven at 75 °C with ambient pressure for 4.5h.

To make a pellet, ~15 mg of CMPs (**CTPA** and **STPA**) sample was put into a 3 mm inner-diameter 40mm length cell and was tightly packed. The measurements were carried out using Keithley 6510 DAQ semiconductor parameter analyzer. The electric conductivity was performed by two-probe measurement by pressing the sample powder. Current-voltage (*I*-*V*) curves were plotted at 25 °C in vacuum.

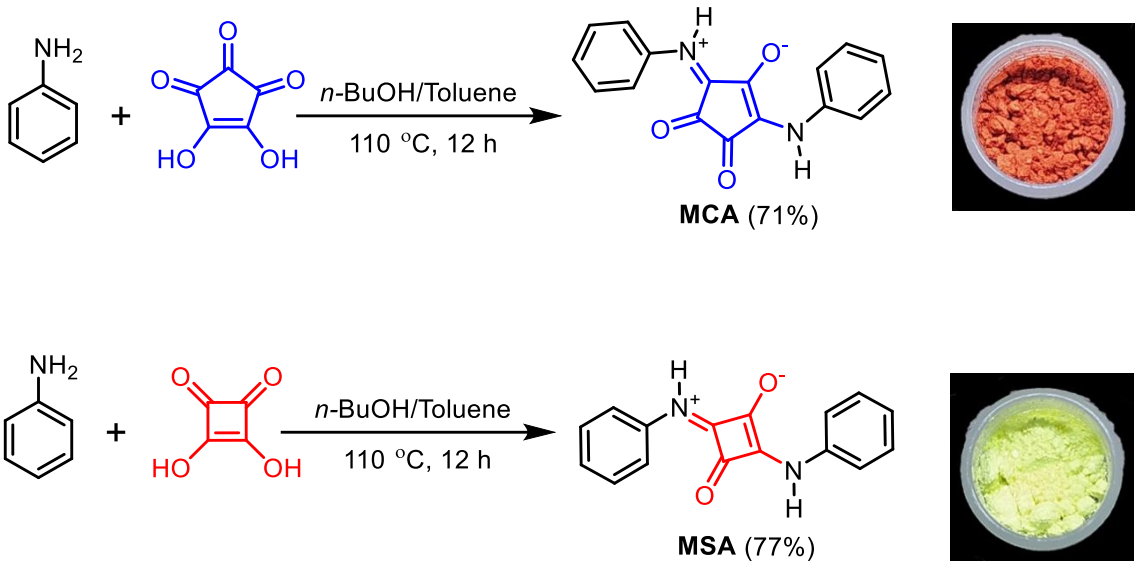
Cyclic voltammetry (CV) experiment:

These measurements were carried out using instrument potentiostat Interface 1010E 31184 in three-electrode electrochemical cell with scan rate of 10 mV/s. The measurements were performed using anhydrous acetonitrile (for CMPs and model molecules) with Tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Pt wire was used as auxiliary electrode. Ag/AgCl as reference electrode and glassy carbon electrode as working electrode. CMPs were dispersed in the solution and the measurement were made immediately. Ferrocene oxidation was measured for internal calibration before each measurement.

Experimental section:

Synthesis of model compounds (MCA and MSA):

The mixture of croconic/squaric acid (CA/SA) (50 mg, 1 equiv, 0.352 mmol/0.438 mmol) and aniline (0.321 mL, 10 equiv, 3.52 mmol/4.38 mmol) in n-butanol/toluene (2 mL, 1:1 in vol) was degassed using nitrogen gas over 30 min. The degassed mixture was stirred at 110 °C for 12 h. The reaction mixture was filtered, washed with chloroform (30 mL) followed by petroleum ether (15 mL), and dried in a vacuum at 80 °C; a solid product was obtained with 71-77% yield. The formation of the compounds is confirmed through ^{1}H and ^{13}C-NMR.[2,3]



Scheme S1: Synthesis of **MCA** and **MSA.**

MCA: Red solid with 71% yield.

^{1}H NMR (400 MHz, DMSO-d6): 11.51 (s, 2H, R_2NH), 7.20-7.47 (m, 10H, ArH).

^{13}C NMR (100 MHz, DMSO-d6): 190.10, 177.22, 139.44, 137.13, 130.73, 129.16, 128.88, 127.84, 126.38, 125.50, 124.34, 123.44, 122.01.

MSA: Yellow solid with 77% yield.

^{1}H NMR (400 MHz, DMSO-d6): 10.87 (s, 2H, R_2NH), 7.00-7.78 (m, 10H, ArH).

^{13}C NMR (100 MHz, DMSO-d6): 186.83, 174.92, 140.49, 140.23, 129.92, 129.43, 124.97, 122.83, 122.16, 119.27, 118.59, 117.98

Synthesis of CTPA and STPA:

Croconic acid (CA) (0.20 mmol) / Squaric acid (SA) (0.26 mmol) and N^1,N^1-bis(4-aminophenyl) benzene-1,4-diamine (TPA-NH_2) (0.18 mmol) in *n*-butanol/*o*-dichloro-benzene (6 mL, 1/1 in vol) was degassed in pressure tube (15 mL) using nitrogen gas over 30 min. The pressure tube was sealed off and heated at 80 °C for 5 days. The reaction mixture was filtered and washed with THF (40 mL) followed by chloroform (20 mL). The obtained residue was purified by soxhlet distillation using THF followed by chloroform for 12h each and dried under vacuum (low to high) for 12h and further heat dried under vacuum at 100 °C for 6h to give a solid with 96% and 94% yield respectively.

List of Donor and Acceptor Groups.

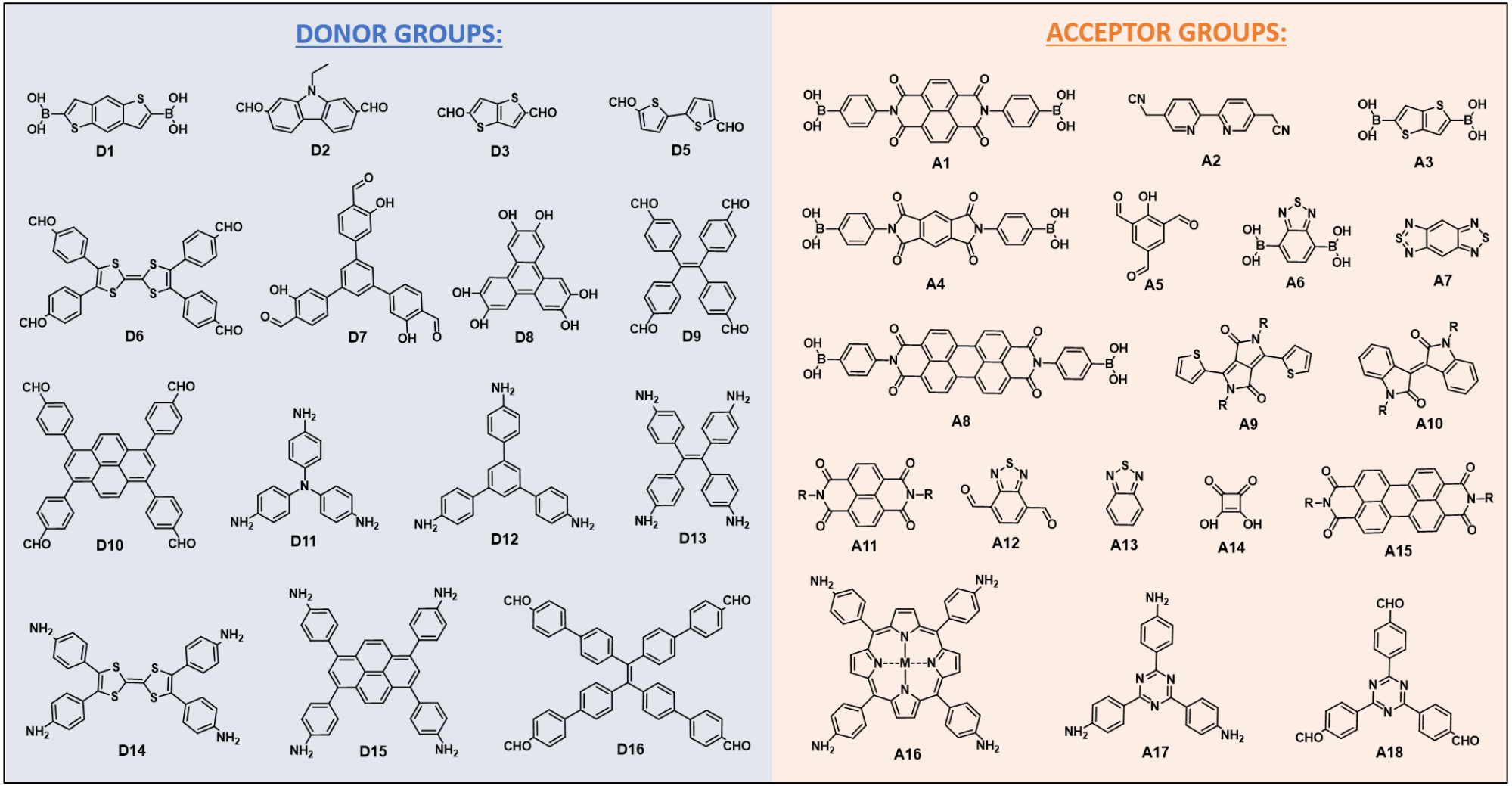


Chart S1: List of Donor and Acceptor Groups.

Section 1: NMR spectrum of Model molecules

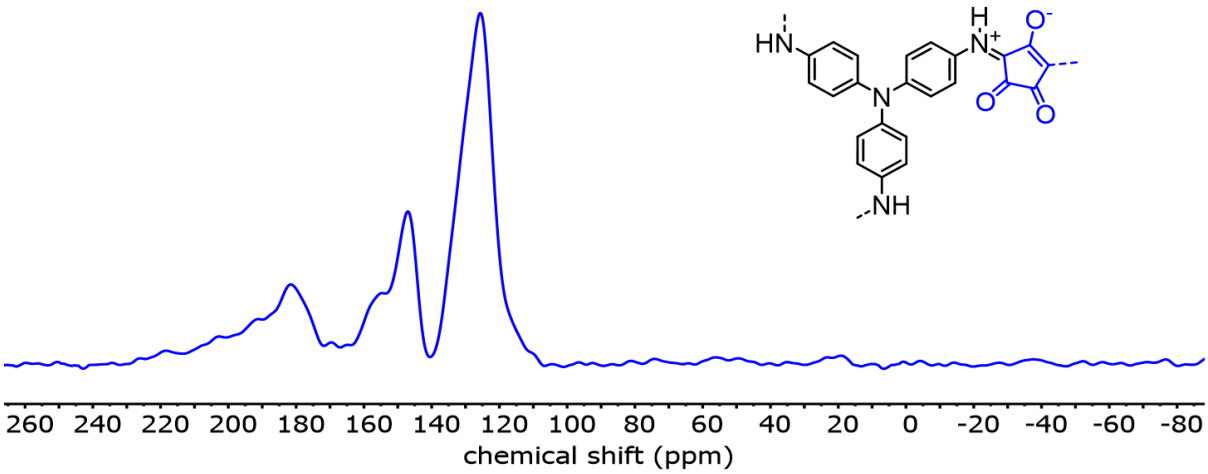


Figure S1: ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR of **CTPA.**

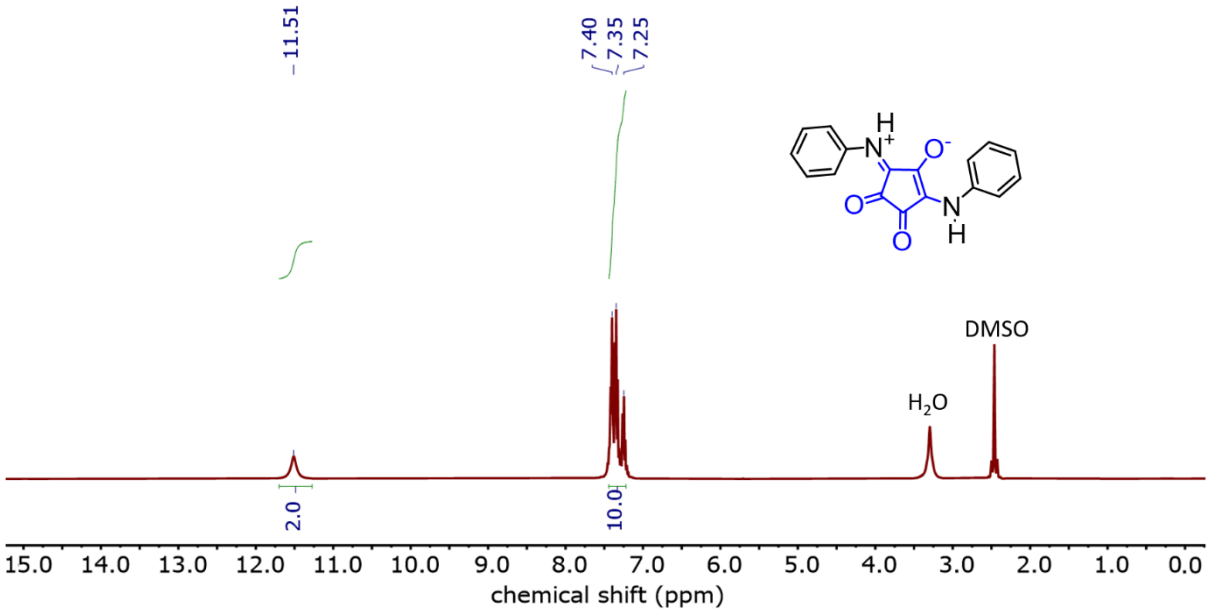


Figure S2: ^{1}H-NMR of **MCA** (DMSO-d6).

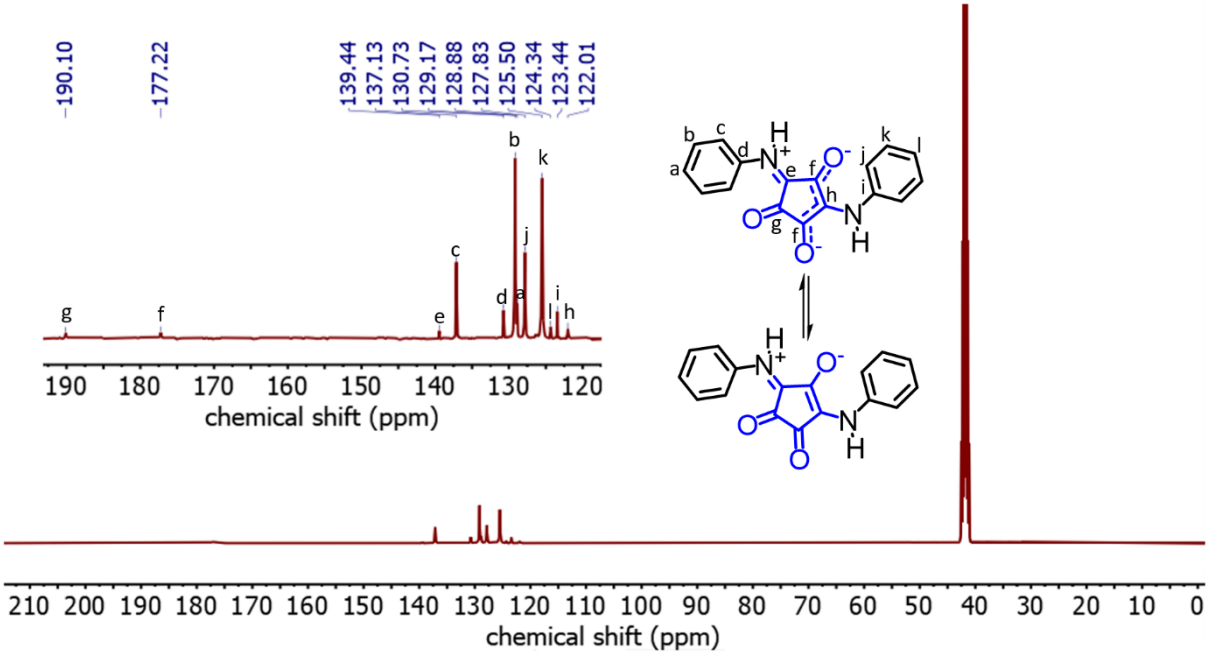


Figure S3: ^{13}C-NMR of **MCA** (DMSO-d6). Tentative assignment of signals was done based on the electronic arrangement.

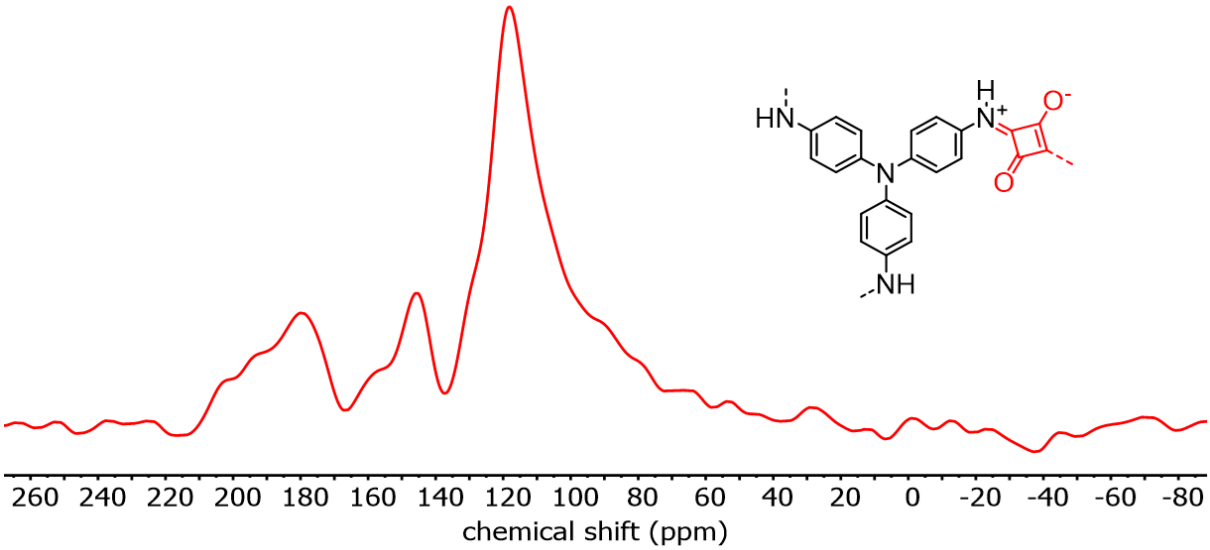


Figure S4: ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR of **STPA.**

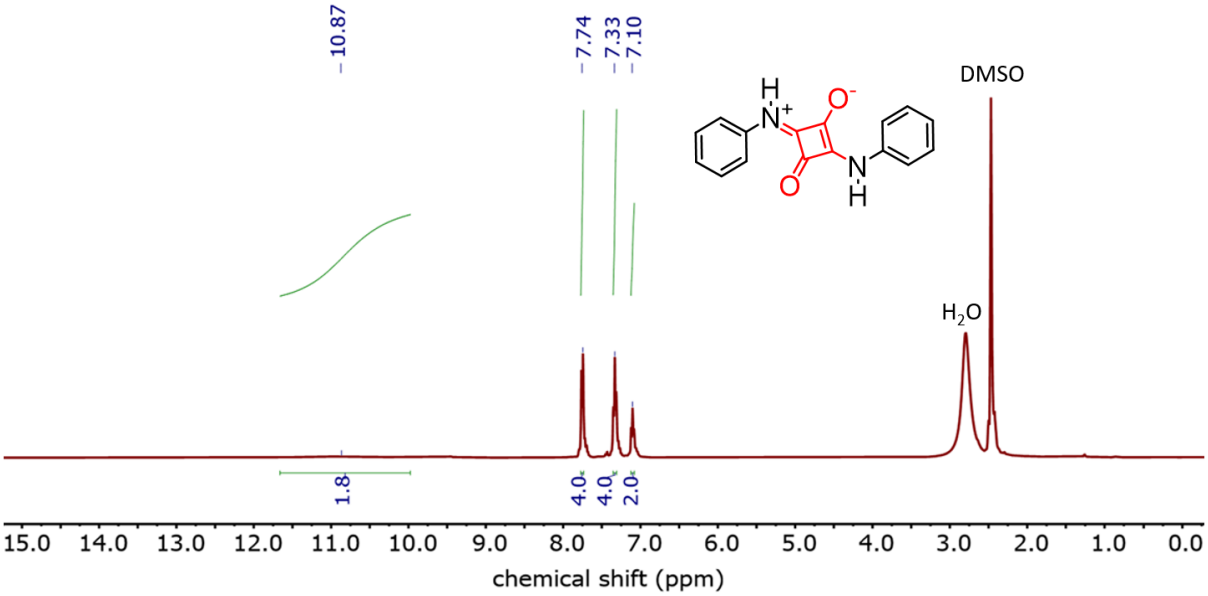


Figure S5: ^{1}H-NMR of **MSA** (DMSO-d6).

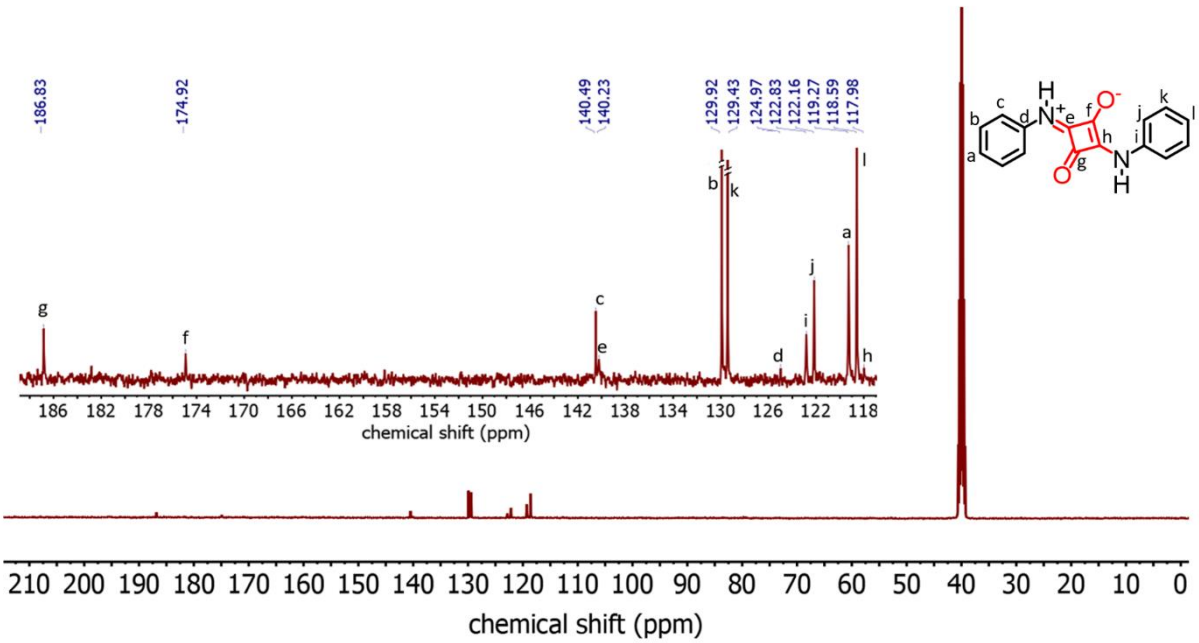


Figure S6: ^{13}C-NMR of **MSA** (DMSO-d6). Tentative assignment of signals was done based on the electronic arrangement.

Section 2: X-ray Photoelectron Spectroscopy (XPS)

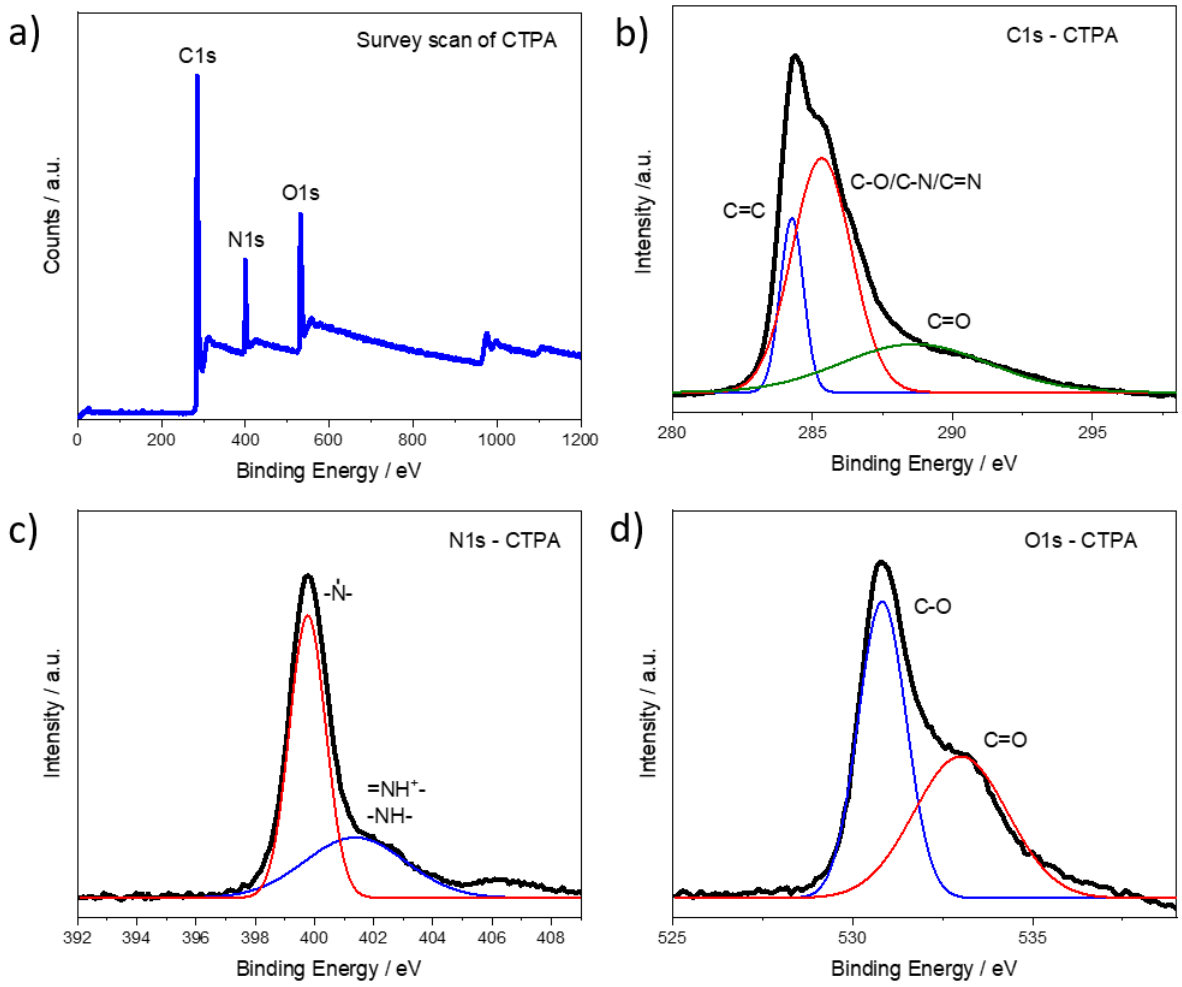


Figure S7: a) XPS survey spectrum of **CTPA**, b) High resolution C1s spectrum (black) and corresponding peak deconvolution (colour). c) High resolution N1s spectrum (black) and corresponding peak deconvolution (colour). d) High resolution O1s spectrum (black) and corresponding peak deconvolution (colour).

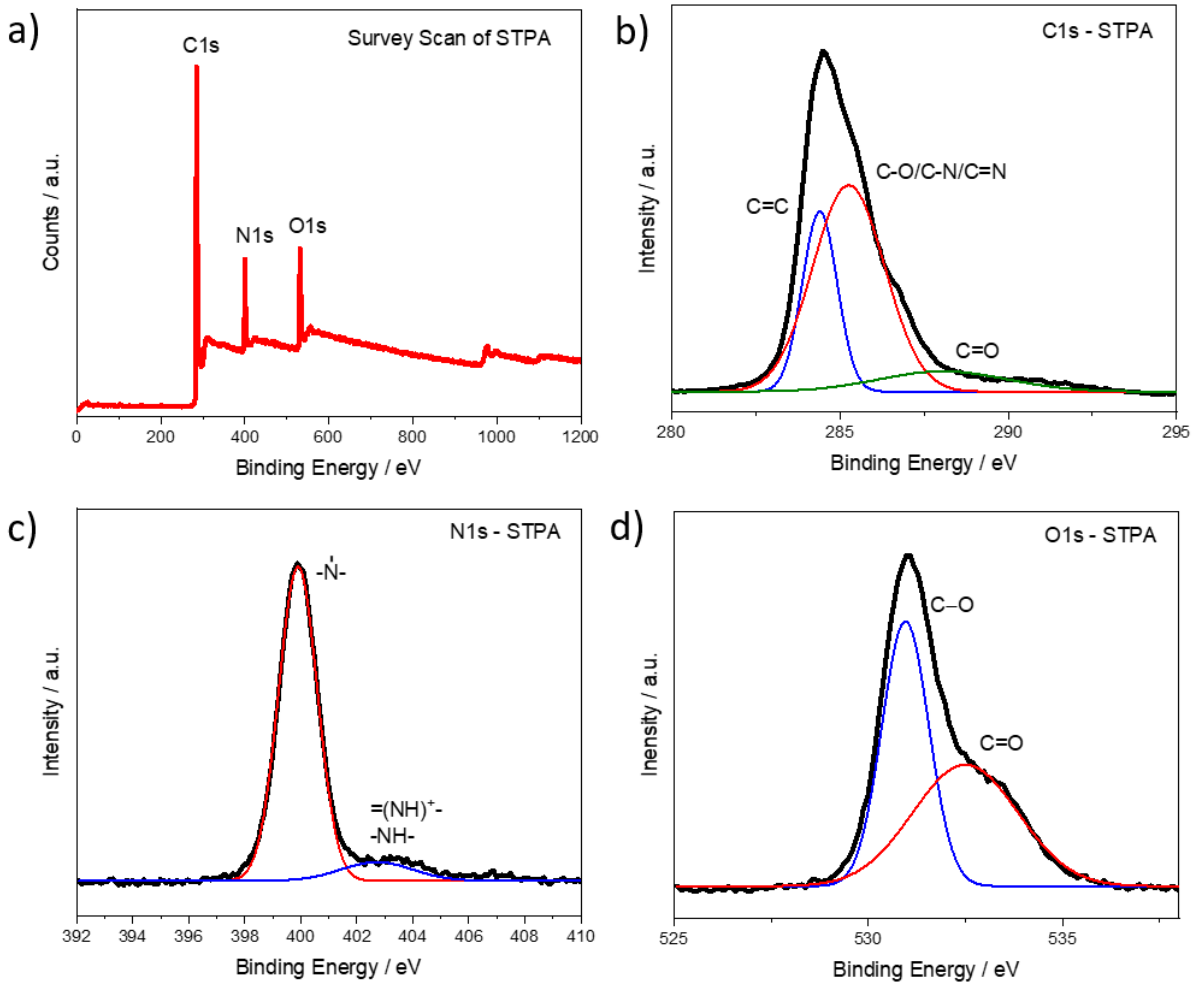


Figure S8: a) Survey spectrum of **STPA**, b) High resolution C1s spectrum (black) and corresponding peak deconvolution (colour). c) High resolution N1s spectrum (black) and corresponding peak deconvolution (colour). d) High resolution O1s spectrum (black) and corresponding peak deconvolution (colour).

The unit cell of the synthesized CMPs has a formula of $C_{41}H_{27}N_8O_3$ and $C_{40}H_{27}N_8O_2$ for **CTPA** and **STPA**, respectively. And theoretical atomic ration of C:N:O of 41:8:3 for **CTPA** and 20:4:1 for **STPA**. The slightly increased nitrogen and oxygen content may be due to the moisture.

	CTPA		STPA	
	Expected Atomic %	**XPS survey Atomic %**	**Expected Atomic %**	**XPS survey Atomic %**
C	78.7	74.82	80	77.42
N	15.5	10.72	16	11.62
O	5.8	14.46	4	10.96

Table S1: Atomic concentration of the C, N, O elements in the **CTPA** and **STPA** CMPs respectively

The peaks of C1s, N1s and O1s appeared in the broad scan XPS survey spectrum of both **CTPA** and **STPA** (Fig S7a, Fig S8a), In high resolution C1s spectra, the three peaks with binding energy at 284.2, 285.4 and 288.6 eV correspond to C=C, C-O/C-N/C=N and C=O, respectively of **CTPA** (Fig S7b). Similarly, three peaks with binding energy 284.4, 285.2 and 288.0 eV correspond to C=C, C-O/C-N/C=N and C=O, respectively of **STPA** (Fig S8b).

The N1s bands was deconvoluted into two peaks with binding energy of 399.8 and 401.4 eV which is from tertiary amine nitrogen of TPA and $=(NH)^{+}$- / -NH- respectively for **CTPA** (Fig S7c) and 399.8 and 402.6 eV corresponds to tertiary amine nitrogen of TPA and $=(NH)^{+}$- / -NH- respectively for **STPA**. (Fig S8c)

The deconvoluted high resolution O1s spectrum shows two peak with binding energy at 530.8 and 533.0 eV corresponds to C-O and C=O respectively in **CTPA** (Fig S7d) and 530.9 and 532.6 eV respectively in **STPA** (Fig S8d)

Slight variation in composition may originate from the hydrocarbon impurities from the air and moisture (commonly seen in XPS)

Section 3: PXRD pattern

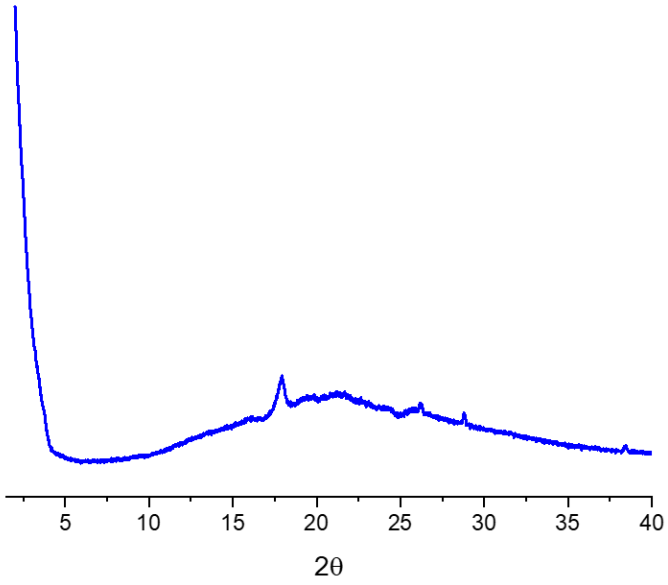


Figure S9: PXRD spectrum of **CTPA.**

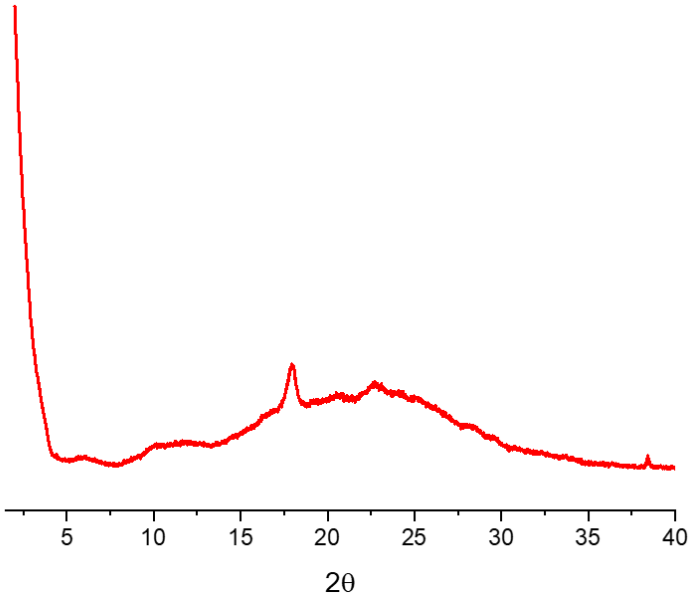


Figure S10: PXRD spectrum of **STPA.**

Section 4: TGA pattern

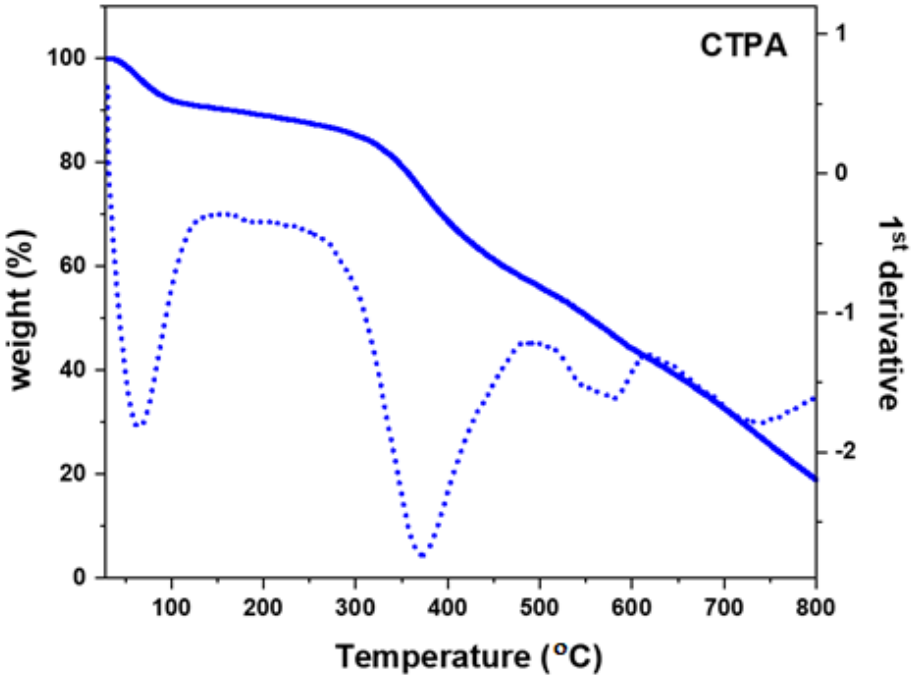


Figure S11: Thermogravimetric analysis (TGA) curve of **CTPA** under heating rate of 10 °C min^{-1}.

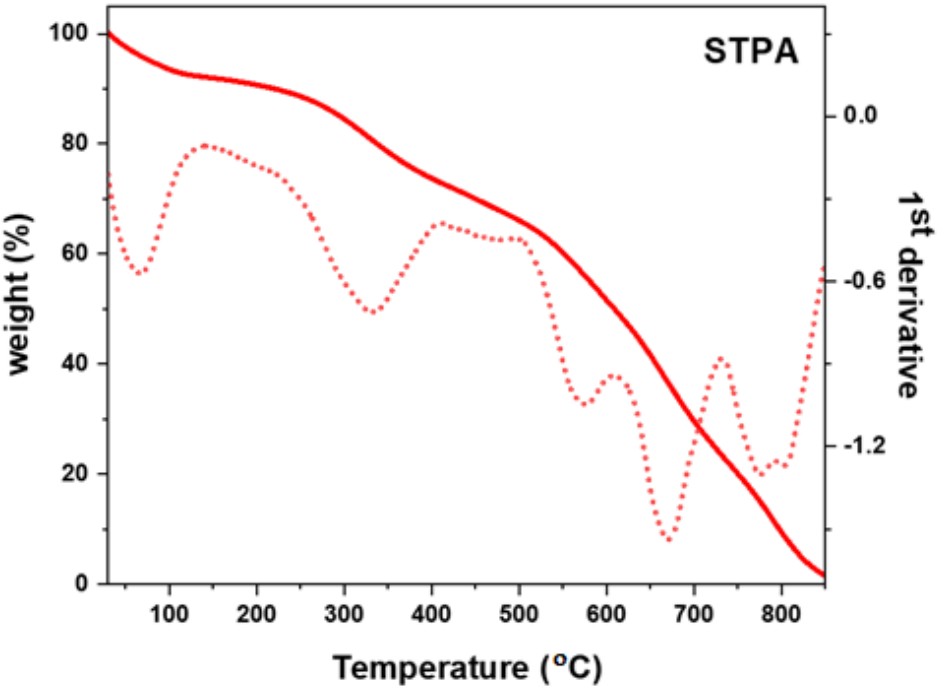


Figure S12: Thermogravimetric analysis (TGA) curve of **STPA** under heating rate of 10 °C min^{-1}.

Section 5: SEM images

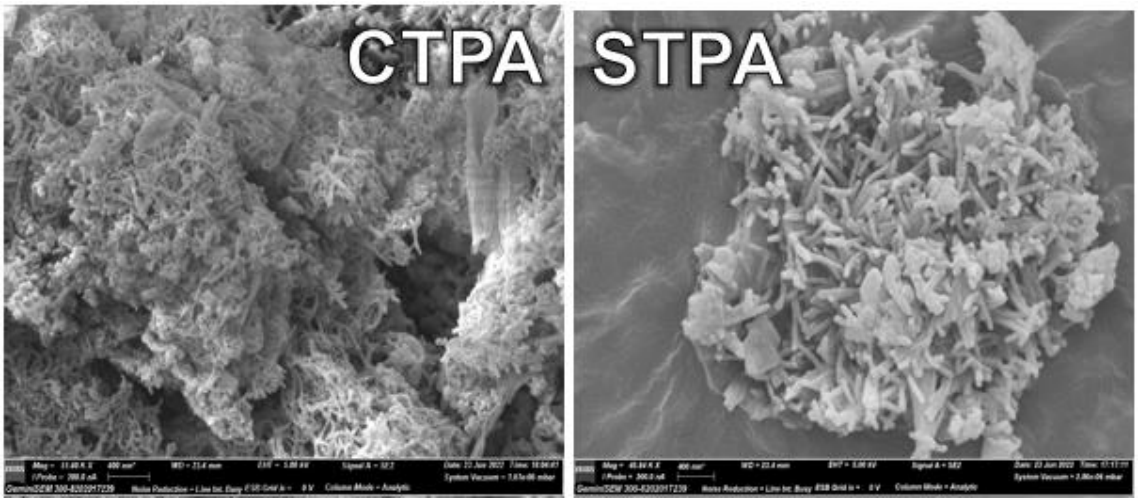


Figure S13: SEM images of **CTPA** (left) and **STPA** (right) at 400 nm scale.

Section 6: UV-Vis and Cyclovoltammetry studies

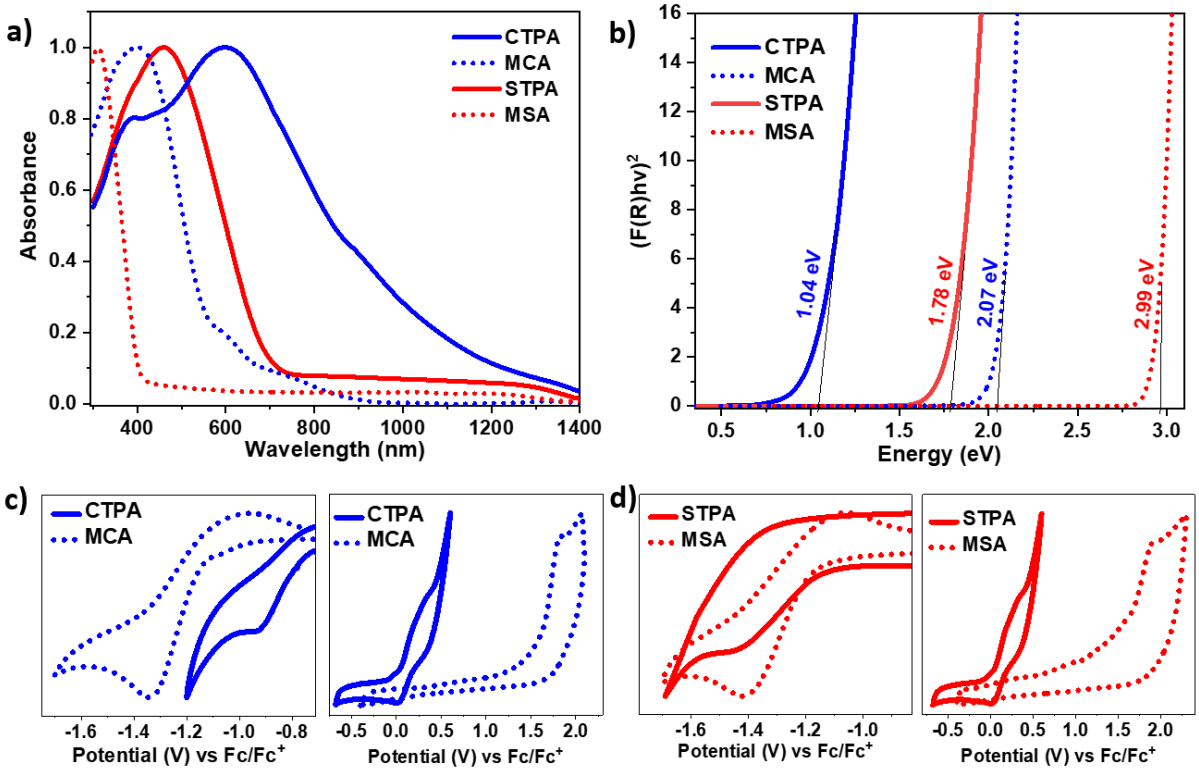


Figure S14: a) Diffuse reflectance spectra of CMPs (**CTPA** and **STPA**) along with its model molecules (**MCA** and **MSA**); b) Kubelka-Munk function; c) Cyclic voltammograms of **CTPA** and **MCA**; d) Cyclic voltammograms of **STPA** and **MSA.**

Section 7: HOMO and LUMO levels of Model compound

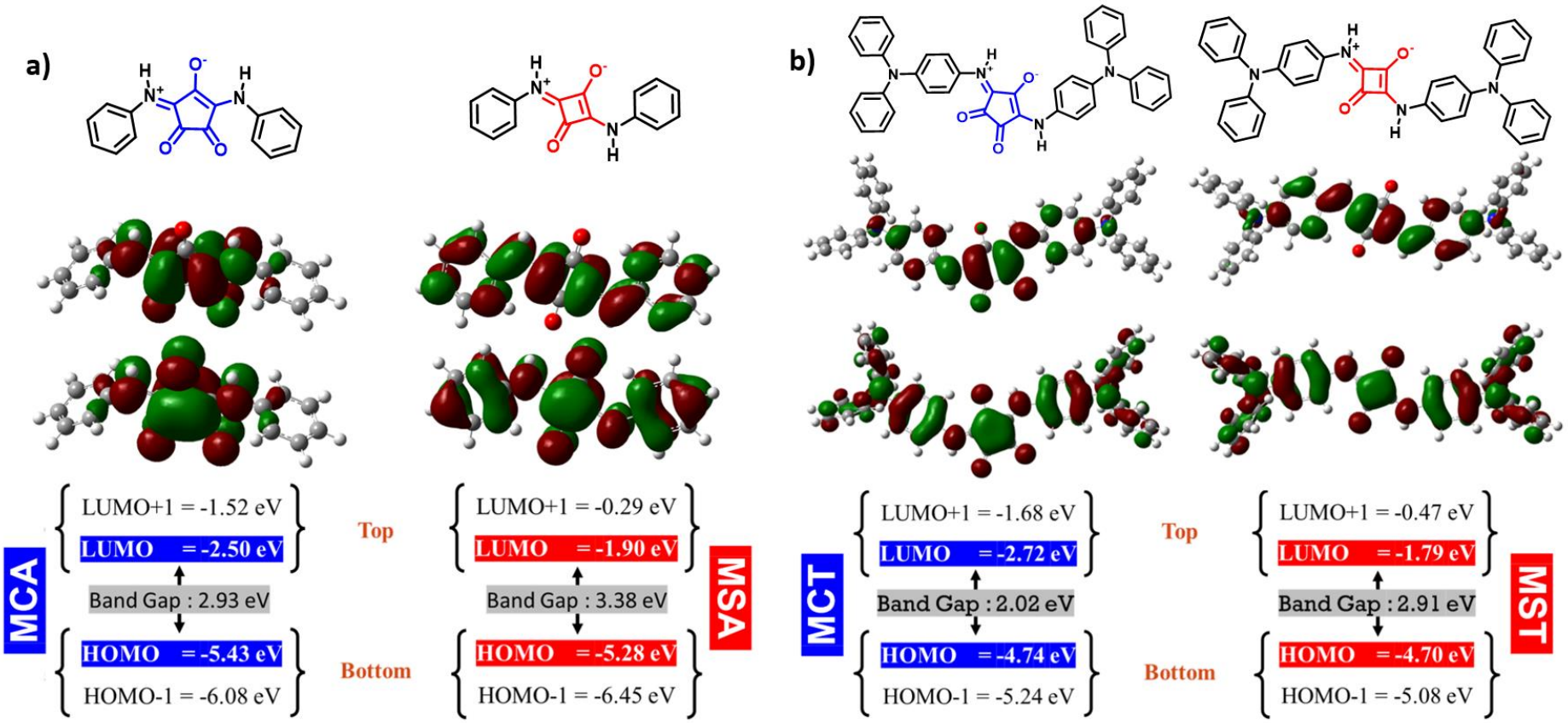
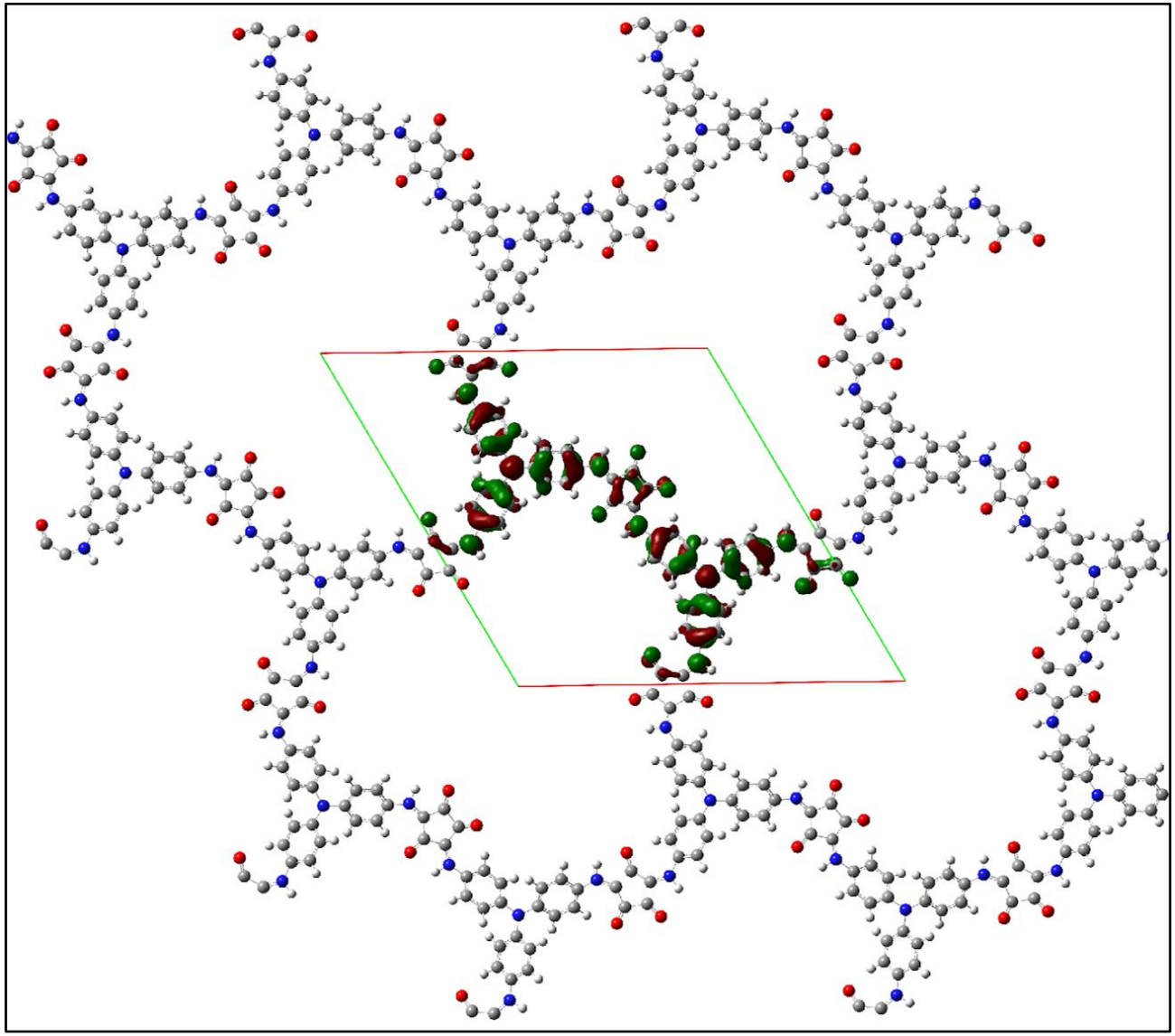


Figure S15: a) HOMO and LUMO enery levels of **MCA** and **MSA**; b) HOMO and LUMO levels of **MCT** and **MST**.

Section 8: HOCO and LUCO levels of CTPA



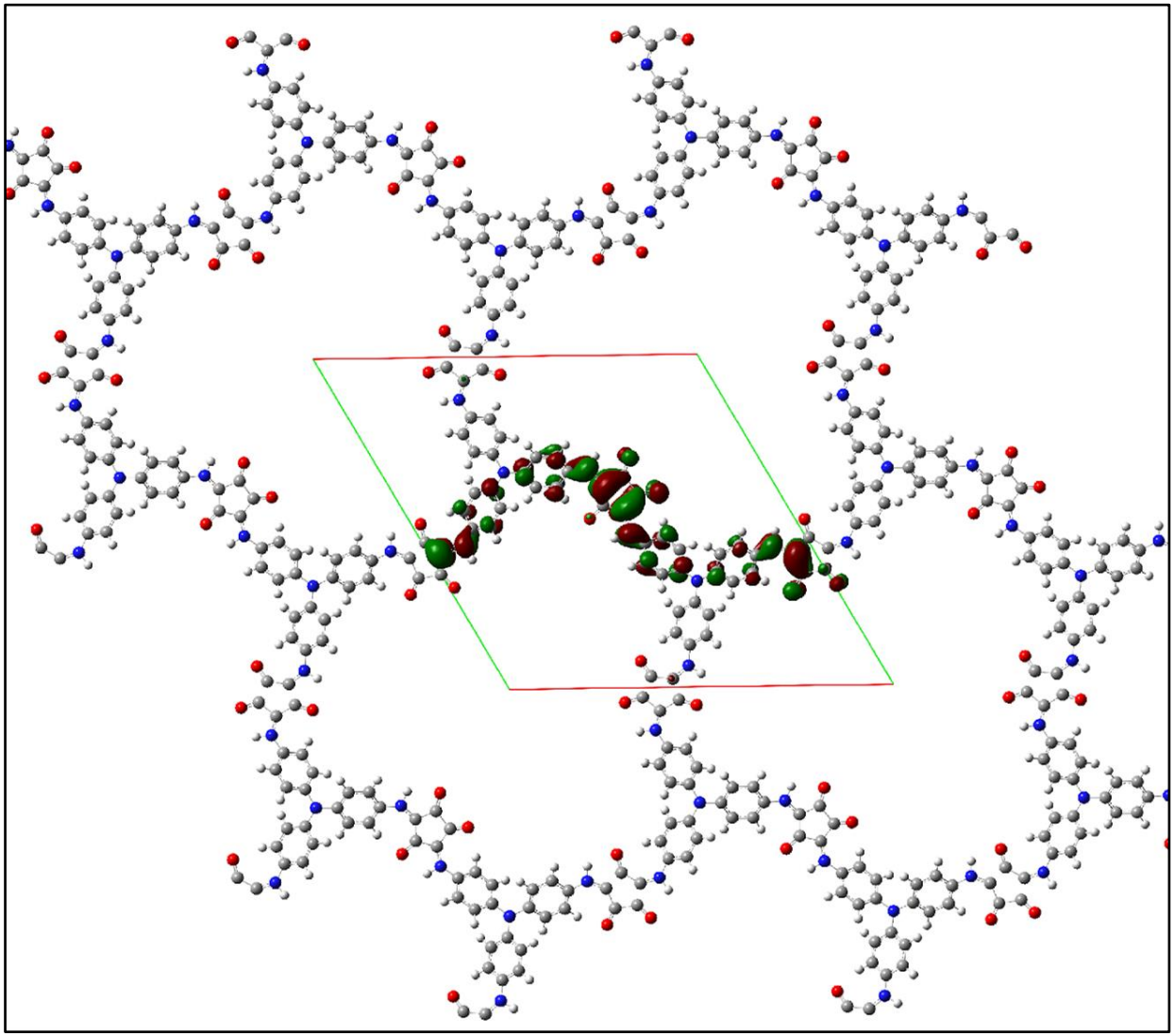
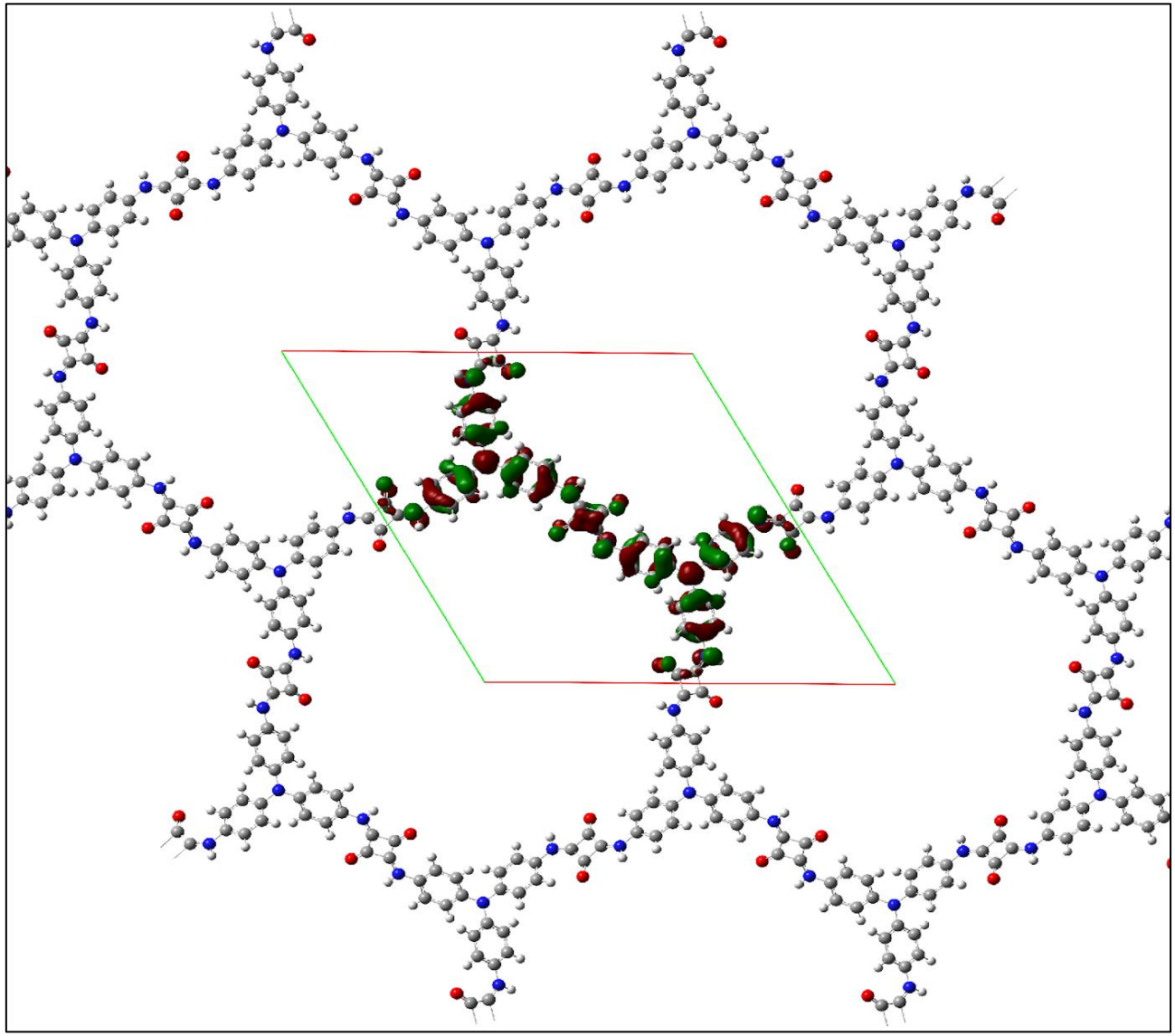


Figure S16: Degenerated HOCO = -4.389 eV; HOCO-1 = -5.067 eV (top) and degenerated LUCO = -3.582 eV; LUCO+1 = -3.583 eV (bottom) of **CTPA** and Band gap = 0.81 eV.

Section 9: HOCO and LUCO levels of STPA



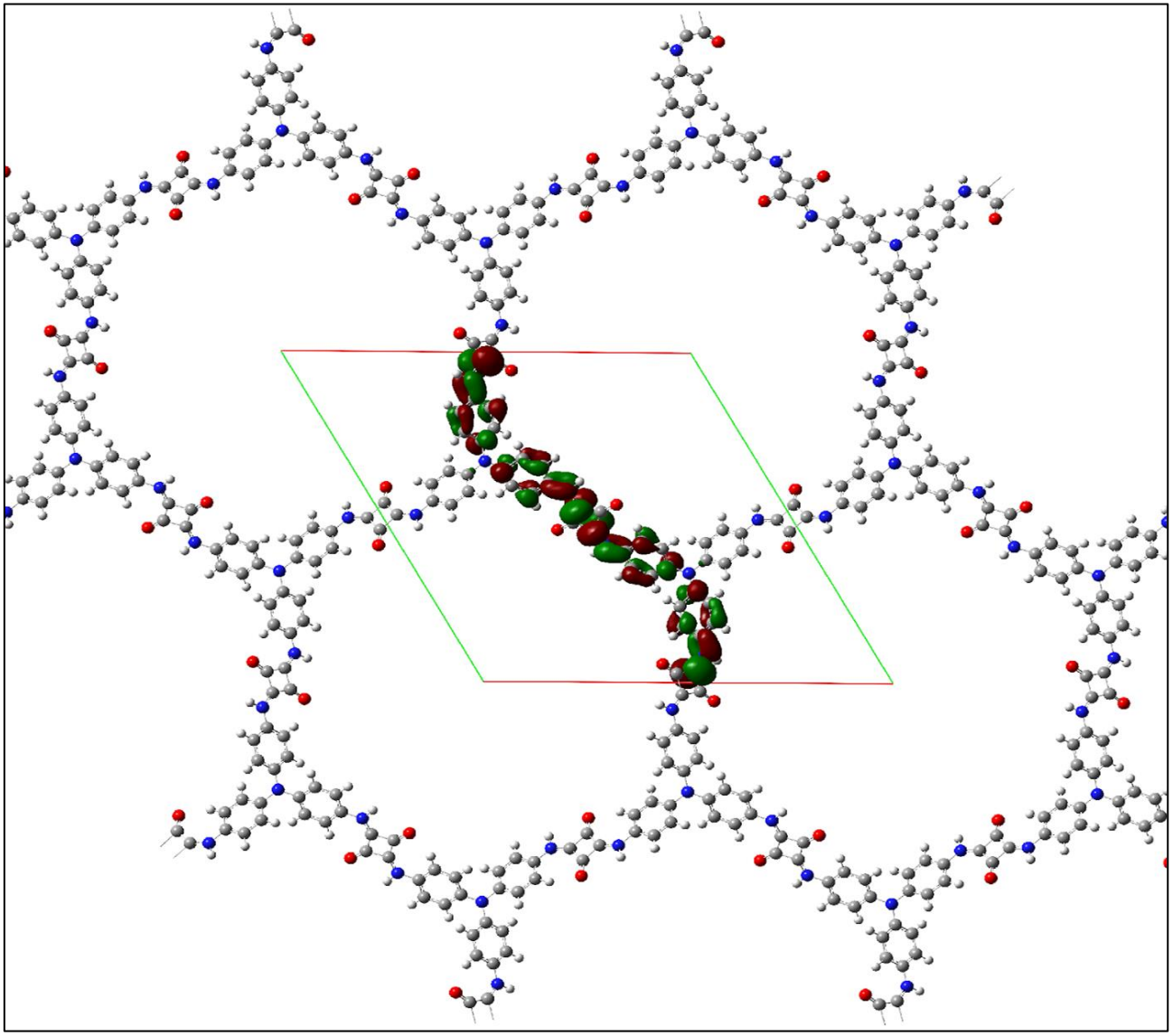


Figure S17: Degenerated HOCO = -4.953 eV; HOCO-1 = -4.153 eV(top) and degenerated LUCO = -2.712 eV; LUCO+1 = -3.512 eV(bottom) of **STPA** and Band gap = 1.4 eV.

Section 10: FT-IR COMPARISON

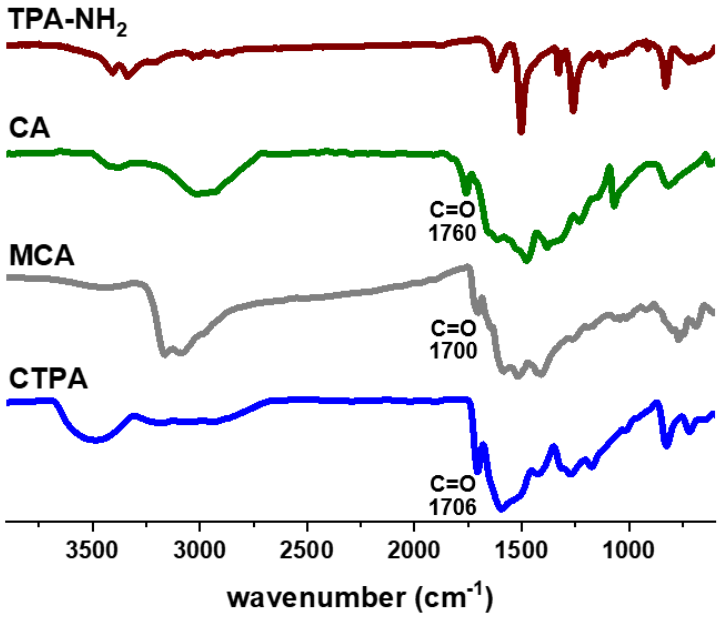


Figure S18: FT-IR spectra of **CTPA, MCA, CA** and **TPA-NH2**.

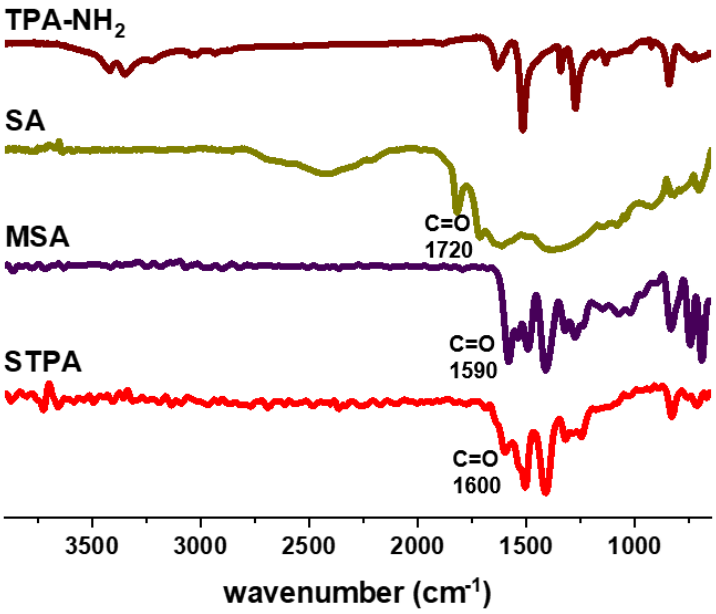


Figure S19: FT-IR spectra - of **STPA, MSA, SA** and **TPA-NH2**.

References:

1 Q. Sun, B. Aguila, J. Perman, L. D. Earl, C. W. Abney, Y. Cheng, H. Wei, N. Nguyen, L. Wojtas and S. Ma, *J. Am. Chem. Soc.*, 2017, **139**, 2786–2793.

2 F. Jansen, M. Lamla, D. Mauthe, S. Fischer, H. Barth, A. J. C Kuehne, F. Jansen, A. J. C Kuehne, M. Lamla, D. Mauthe, S. Fischer and H. Barth, *Macromol. Rapid Commun.*, 2020, **41**, 2000418.

3 M. Vega, R. M. Gomila, J. Pons, A. Frontera, C. Rotger and A. Costa, *Dye. Pigment.*, 2022, **207**, 110746.