

Unveiling the Electronic Properties of Metal-free and Undoped Covalent organic framework as a Semiconductor

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S1. Chemicals and Materials

The following chemicals were purchased from Sigma Aldrich, USA:

Cyanuric chloride ($C_3Cl_3N_3$, 99%), 1,4-Dioxane ($C_4H_8O_2$, ACS reagent, $\geq 99\%$), Mesitylene ($C_6H_3(CH_3)_3$, 98%), p-Phenylenediamine ($C_6H_4(NH_2)_2$, $\geq 99\%$ GC/NT), 4-Hydroxybenzaldehyde (HOC_6H_4CHO , 98%), Methanol (CH_3OH , ACS reagent, $\geq 99.8\%$), Acetic acid (CH_3CO_2H , glacial, ACS reagent, $\geq 99.7\%$), Sodium hydroxide (NaOH, ACS reagent, $\geq 97\%$ pellets) and Acetone (CH_3COCH_3 , ACS reagent, $\geq 99.5\%$). Each solvent was attained commercially and used exactly as it was given. All aqueous solutions were prepared using double-distilled water.

S2. Characterization techniques

The Fourier Transform Infrared (FTIR) spectroscopy was carried out using a Perkin Elmer FTIR spectrometer (Model: Spectrum RXI-Mid IR) with a 4000-400 cm^{-1} range. The Quantachrome BET surface area analyzer (Model: Autosorb iQ Station 1) was used to collect the nitrogen adsorption-desorption data at 77 K. Before the analysis, samples were degassed at 120 °C for 8 hours. The powder X-ray diffraction (PXRD) data was collected using a monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) source on a Rigaku Benchtop X-ray diffractometer (Model: MiniFlex II, Japan). Utilizing a Carl Zeiss Field-Emission Scanning Electron Microscope (Model: Carl Zeiss Ultra Plus), the three-dimensional morphology was studied. Thermo Scientific Cryo-TEM (Model: Talos Arctica) was used for the two-dimensional morphological analysis. The thermal stability of the product was analyzed using the Thermo Gravimetric Analysis instrument (Model: Mettler Toledo). The chemical compositions of the material were analyzed using X-ray photoelectron spectroscopy (Model: PHI 5000 VersaProbe III). The valence band maxima and conduction band minima were characterized through Ultraviolet photoelectron spectroscopy (Model: PHI 5000 VersaProbe III). The band gap calculations were carried out using Cyclic voltammetry (Model: PalmSens 3) and Ultraviolet spectroscopy (Model: Specord 210 plus). The synthesized product was analyzed via 1H and ^{13}C Nuclear magnetic resonance (NMR) spectra recorded on Jeol 400 MHz FT NMR spectrometer (Model: JNM-EXCP 400) in $CDCl_3$ or DMSO- d_6 solvent. Tetramethylsilane, the internal standard, is referenced in the chemical shift values, which are expressed in ppm.

S3. Experimental Procedures

Synthesis of 2,4,6-tris-(*p*-formylphenoxy)1,3,5-triazine (TFPT)

An oven-dried 250 ml round bottom flask containing a magnetic bead was charged with a solution of 4-hydroxybenzaldehyde (3.66 g, 30 mmol) in 50 ml water and NaOH (1.2 g, 30 mmol). This reaction mixture was continuously stirred at 0 °C while a solution of cyanuric chloride (1.84 g, 10 mmol) in 50

ml acetone was added dropwise to it. The resulting mixture was stirred at room temperature for 3 h. After this, the mixture was vacuum filtered, washed with water, and dried at 70 °C for 5 h to obtain a white solid product (Yield: 91%). The sample was characterized using ^1H and ^{13}C NMR spectroscopies (Figures S1 & S2).

Synthesis of PPDA-TFPT-COF

The material was synthesized by Schiff-base reaction. An accurately weighed amount of monomers, TFPT (441.39 mg, 1 mmol) and *p*-phenylenediamine (PPDA) (162.21 mg, 1.5 mmol) were dissolved in a mixture of mesitylene/ 1,4-dioxane (1:3 v/v, 40 ml). Then, acetic acid (aq., 6 M, 1 ml) was added to the reaction mixture and placed in a 100ml Teflon autoclave. After this, the autoclave was flushed with nitrogen for about 30 min, sealed, and heated at 120 °C for 72h. After 72h, the obtained brown precipitate was collected by vacuum filtration and washed successively with acetone, 1,4-dioxane, methanol, and water, and dried at 120 °C overnight (Yield: 89%).

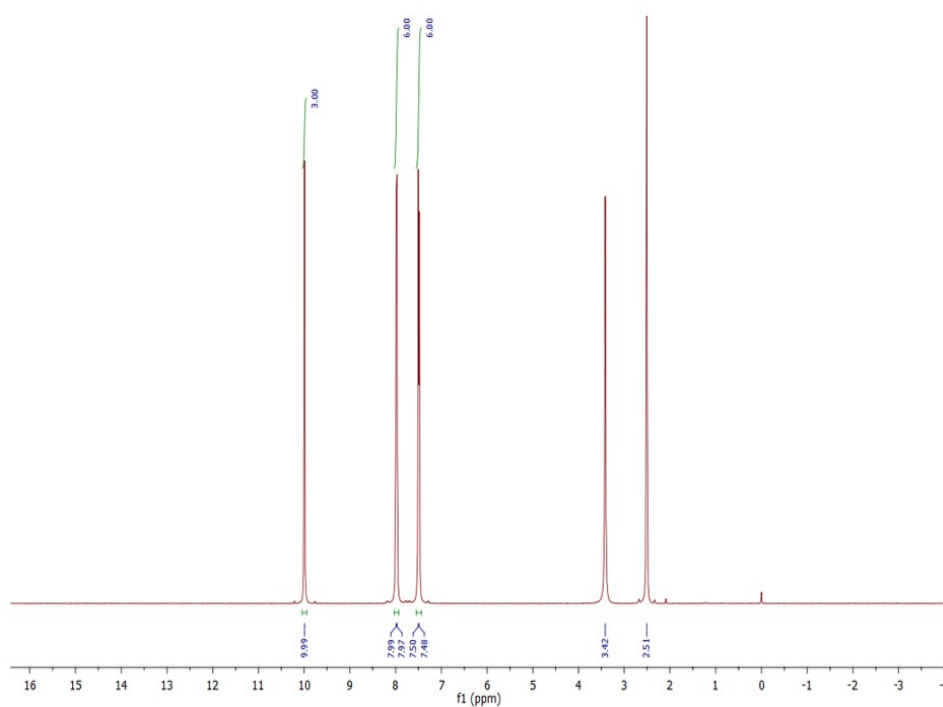


Figure S1. ^1H NMR spectra of 2,4,6-tris-(*p*-formylphenoxy)1,3,5-triazine (TFPT) precursor.

Light brown solid powder ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ (ppm): 9.99 (s, 3H), 7.98 (d, $J = 8.2$ Hz, 6H), 7.49 (d, $J = 8.1$ Hz, 6H).

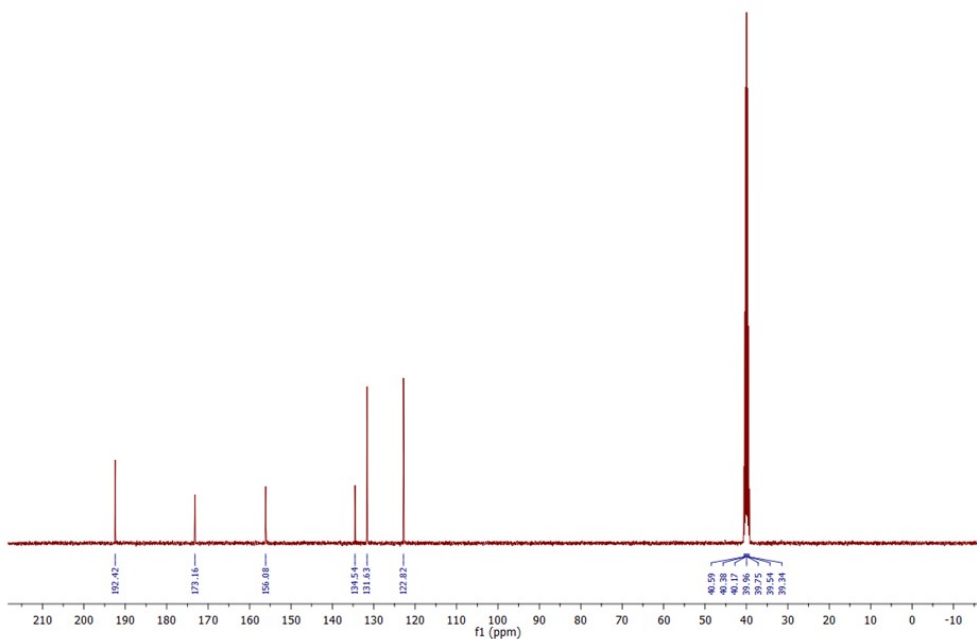


Figure S2. ^{13}C NMR spectra of 2,4,6-tris-(*p*-formylphenoxy)1,3,5-triazine (TFPT) precursor.

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): 192.42, 173.16, 156.08, 134.54, 131.63, 122.82.

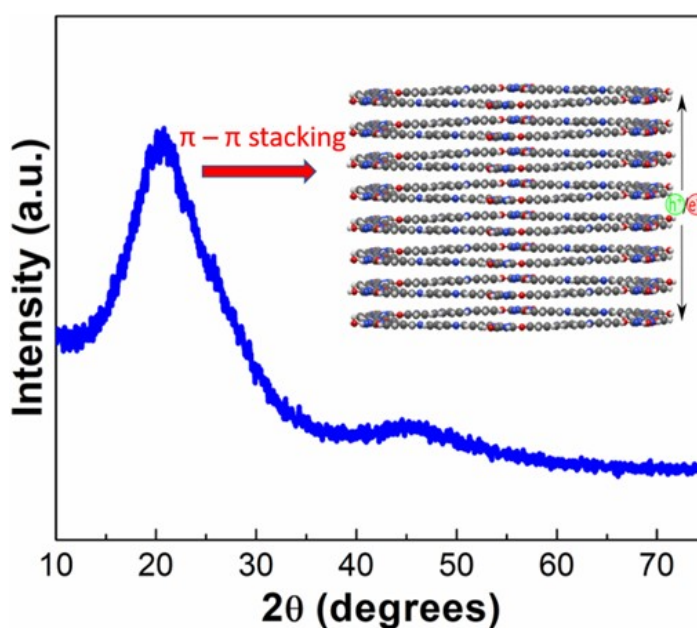


Figure S3. PXRD pattern of PPDA-TFPT-COF with π - π stacking.

The structural regularity of PPDA-TFPT-COF was evaluated through powder X-ray diffraction (PXRD).

The PXRD pattern of PPDA-TFPT-COF showed two broad peaks demonstrating the amorphous nature of the material which insinuates the angular strain between the precursors leading to the random

orientation of the layers and creation of dynamic covalent bonds (Figure S3).¹ The angle strain between the C3 symmetric precursors prevented the formation of a symmetric framework geometry due to this the broad pattern indicates a lack of ordered arrangement of the polymer structure. Further, the broad peak at $2\theta = 13.2-29.9^\circ$ is attributed to the $\pi-\pi$ stacking and states the presence of triazine core in PPDA-TFPT-COF.^{2,3} A small, broad peak in the powder X-ray diffraction (PXRD) pattern was observed at $2\theta = 43.5-46.8^\circ$, indicating the presence of a turbostratic carbon structure in the material.⁴ The appearance of this peak supports the conclusion that the material has a partially ordered arrangement, with a mix of both crystalline and amorphous regions.

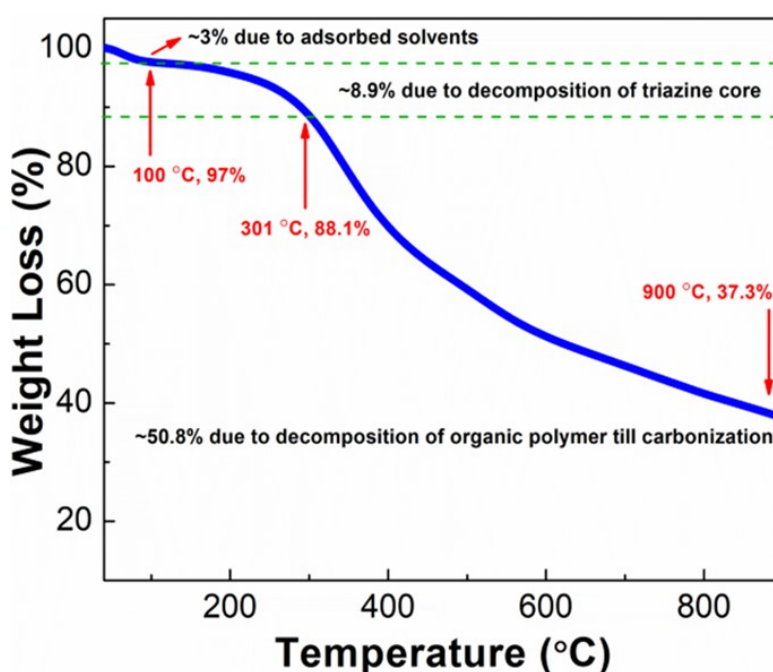


Figure S4. Thermogravimetric analysis of PPDA-TFPT-COF in air atmosphere.

The thermal stability of PPDA-TFPT-COF was evaluated via thermogravimetric analysis (TGA) in the air atmosphere. The initial minor weight loss of ~3% to 100 °C may be attributed to the solvent or guest molecules adsorbed on the surface of PPDA-TFPT-COF. The next weight loss stage of ~8.9% from 100-301 °C occurs due to the decomposition of the triazine core. The final and major weight loss of ~50.8% from 301-900 °C occurs due to the complete decomposition of the organic polymer and residues.⁵

S4. Theoretical calculations:

We have focused our theoretical calculation on the PPDA-TFPT-COF ring monomer which makes up a significant part of the polymer. The monomer comprises 276 atoms, which makes it difficult to optimize the molecule's ground state using quantum mechanical methods. The best way to tackle this problem is the use of classical methods to optimize the molecule. We started the calculation using the planar PPDA-TFPT-COF ring monomer and optimize it using a universal force field (UFF).⁶ This was implemented using Avogadro software.⁷ The XYZ coordinates (in angstrom) for the optimized structure are shown in table S2.

Excited state calculations were performed using time-dependent density functional theory (TD-DFT) with the hybrid B3LYP functional⁸ and 6-31G* basis set. B3LYP is a hybrid functional which uses approximations to the exchange-correlation energy functional in DFT. B3LYP functional was evaluated for a wide range of chemical substances and produced consistent findings.⁹ The excited state analysis of the PPDA-TFPT-COF monomer is shown in Table S1 and shows the excited state energies for the first 10 excited singlet states. The first excited state (S1) has an excitation energy of 3.02 eV followed by the two degenerated states (S2 and S3) at 3.09 eV. S1 is the dark state (zero oscillator strength) and S2 and S3 which are degenerate are the first bright states. S4, S5, S6, and S7 are also dark states. S8 and S9 are the second highest degenerated bright states whereas S10 is again a dark state.

Table S1. Excited state calculation using time-dependent density functional theory (TD-DFT) for the PPDA-TFPT-COF monomer. The calculation was carried out using B3LYP functional and 631G* basis set.

Singlet State	Excitation Energy (eV)	Oscillator Strength	Major MO share %
1	3.0226	0.0	H → L [24], H-1 → L+2 [12], H-2 → L+1 [12]
2	3.0911	6.9914	H-1 → L [24], H → L+1 [13]
3	3.0911	6.9914	H-2 → L [24], H → L+2 [13]
4	3.1930	0.0	H-3 → H-2 → L+2 [12], H-1 → L+1 [12]
5	3.1930	0.0	H-2 → L [29], H-2 → L+1 [12], H-1 → L+2 [12]
6	3.2401	0.0	H-5 → H-4 → L+1 [14], H-3 → L+2 [14]
7	3.3076	0.0	H-1 → L+2 [14], H-1 → L+1 [14]

8	3.3083	0.0401	H → L+2 [20], H-3 → L+2 [15]
9	3.3083	0.0401	H → L+1 [20], H-3 → L+1 [15]
10	3.3093	0.0	H-5 → L+1 [32], H → L+4 [16]

Table S2. Atomic coordinates (in Å unit) of the PPDA-TFPT-COF ring monomer which was used for the TD-DFT calculations.

Atom type	X	Y	Z	Atom type	X	X	Z
O	30.00	-17.70	0	C	65.86	-33.13	0
O	26.73	-14.29	0	C	64.69	-33.91	0
O	25.41	-18.77	0	C	63.45	-33.26	0
O	26.80	-37.30	0	C	63.36	-31.87	0
O	22.21	-38.42	0	C	64.53	-31.09	0
O	25.43	-41.81	0	C	63.49	-28.89	0
O	42.17	-49.87	0	C	65.05	-25.42	0
O	40.85	-54.41	0	C	64.92	-26.81	0
O	45.40	-53.32	0	C	63.65	-27.42	0
O	64.01	-46.25	0	C	62.51	-26.60	0
O	60.74	-42.83	0	C	62.64	-25.21	0
O	65.33	-41.76	0	C	63.90	-24.60	0
O	63.92	-23.24	0	C	67.22	-21.72	0
O	68.51	-22.11	0	C	64.94	-22.34	0
O	65.28	-18.72	0	C	65.55	-20.05	0
O	48.51	-10.71	0	C	63.06	-15.83	0
O	49.90	-6.19	0	C	64.20	-16.63	0
O	45.34	-7.21	0	C	64.11	-18.02	0
N	35.27	-13.97	0	C	62.82	-18.61	0
N	26.11	-16.48	0	C	61.68	-17.81	0
N	28.41	-16.01	0	C	61.79	-16.41	0
N	27.67	-18.23	0	C	60.59	-15.54	0
N	26.04	-25.20	0	C	56.82	-13.32	0
N	26.20	-30.87	0	C	58.07	-13.94	0
N	23.80	-40.06	0	C	58.16	-15.35	0
N	24.54	-37.83	0	C	56.98	-16.10	0
N	26.10	-39.59	0	C	55.73	-15.48	0
N	31.31	-44.48	0	C	55.64	-14.07	0
N	36.31	-47.18	0	C	53.22	-13.88	0

N	43.06	-53.85	0	C	40.25	-9.71	0
N	41.50	-52.10	0	C	49.60	-12.80	0
N	43.80	-51.63	0	C	50.74	-13.60	0
N	50.64	-49.55	0	C	52.02	-13.01	0
N	55.48	-46.57	0	C	52.12	-11.61	0
N	64.63	-44.05	0	C	50.97	-10.81	0
N	62.33	-44.53	0	C	42.99	-7.11	0
N	59.40	-16.06	0	C	41.73	-7.71	0
N	40.11	-10.99	0	C	41.60	-9.10	0
N	54.40	-13.36	0	C	42.77	-9.89	0
N	47.57	-6.74	0	C	44.03	-9.30	0
N	47.00	-9.01	0	C	49.69	-11.40	0
N	49.25	-8.38	0	C	44.16	-7.89	0
C	36.44	-11.85	0	C	46.64	-7.63	0
C	37.61	-11.09	0	C	48.24	-9.38	0
C	38.87	-11.71	0	C	48.94	-7.13	0
C	38.93	-13.11	0	H	35.48	-11.36	0
C	37.76	-13.88	0	H	37.50	-10.01	0
C	36.50	-13.25	0	H	39.89	-13.61	0
C	35.12	-15.25	0	H	37.87	-14.95	0
C	31.33	-15.63	0	H	35.97	-15.92	0
C	32.61	-15.05	0	H	30.50	-14.96	0
C	33.76	-15.85	0	H	32.68	-13.97	0
C	33.62	-17.24	0	H	34.50	-17.88	0
C	32.35	-17.83	0	H	32.27	-18.91	0
C	31.19	-17.04	0	H	23.02	-22.59	0
C	27.05	-15.60	0	H	23.24	-20.15	0
C	28.71	-17.26	0	H	27.54	-20.56	0
C	26.43	-17.87	0	H	27.32	-22.95	0
C	24.01	-22.14	0	H	24.00	-24.83	0
C	24.13	-20.75	0	H	24.04	-29.38	0
C	25.39	-20.14	0	H	23.89	-26.97	0
C	26.54	-20.95	0	H	28.20	-26.69	0
C	26.42	-22.35	0	H	28.35	-29.11	0
C	25.16	-22.96	0	H	28.24	-31.24	0
C	25.00	-24.43	0	H	24.68	-35.50	0
C	24.95	-28.80	0	H	24.91	-33.11	0
C	24.87	-27.41	0	H	29.20	-33.49	0
C	26.04	-26.62	0	H	28.98	-35.94	0
C	27.28	-27.27	0	H	27.55	-45.78	0

C	27.37	-28.67	0	H	25.54	-44.38	0
C	26.20	-29.45	0	H	28.05	-40.86	0
C	27.23	-31.64	0	H	30.01	-42.24	0
C	25.68	-35.11	0	H	29.98	-46.06	0
C	25.81	-33.72	0	H	33.94	-48.30	0
C	27.08	-33.12	0	H	31.77	-47.23	0
C	28.21	-33.93	0	H	33.68	-43.35	0
C	28.09	-35.32	0	H	35.86	-44.43	0
C	26.83	-35.94	0	H	37.65	-45.60	0
C	23.50	-38.81	0	H	39.55	-50.81	0
C	25.78	-38.20	0	H	37.60	-49.42	0
C	25.16	-40.48	0	H	40.08	-45.89	0
C	27.66	-44.71	0	H	42.08	-47.30	0
C	26.51	-43.91	0	H	49.89	-53.47	0
C	26.61	-42.51	0	H	47.67	-54.51	0
C	27.89	-41.92	0	H	45.88	-50.57	0
C	29.04	-42.72	0	H	48.06	-49.57	0
C	28.93	-44.12	0	H	51.35	-51.50	0
C	30.13	-44.99	0	H	55.27	-49.19	0
C	33.89	-47.22	0	H	53.25	-50.53	0
C	32.64	-46.59	0	H	50.85	-46.94	0
C	32.55	-45.19	0	H	52.87	-45.59	0
C	33.73	-44.44	0	H	54.78	-44.62	0
C	34.98	-45.06	0	H	60.25	-45.58	0
C	35.07	-46.47	0	H	58.06	-46.57	0
C	37.49	-46.67	0	H	56.24	-42.66	0
C	39.72	-49.75	0	H	58.47	-41.63	0
C	38.57	-48.94	0	H	67.71	-37.94	0
C	38.69	-47.54	0	H	67.50	-40.39	0
C	39.97	-46.96	0	H	63.19	-39.97	0
C	41.11	-47.77	0	H	63.41	-37.59	0
C	41.00	-49.17	0	H	66.73	-35.70	0
C	41.83	-53.48	0	H	66.69	-31.15	0
C	42.44	-51.21	0	H	66.85	-33.57	0
C	44.11	-52.88	0	H	62.53	-33.85	0
C	49.01	-52.84	0	H	62.38	-31.43	0
C	47.75	-53.43	0	H	62.49	-29.29	0
C	46.58	-52.65	0	H	66.05	-25.03	0
C	46.72	-51.24	0	H	65.82	-27.42	0
C	47.99	-50.65	0	H	61.52	-27.04	0

C	49.15	-51.44	0	H	61.74	-24.60	0
C	50.50	-50.84	0	H	63.17	-14.75	0
C	54.31	-48.69	0	H	65.18	-16.15	0
C	53.14	-49.46	0	H	62.67	-19.68	0
C	51.87	-48.84	0	H	60.71	-18.29	0
C	51.81	-47.44	0	H	60.74	-14.47	0
C	52.98	-46.67	0	H	56.77	-12.24	0
C	54.24	-47.29	0	H	58.94	-13.31	0
C	55.63	-45.29	0	H	57.04	-17.18	0
C	59.41	-44.90	0	H	54.86	-16.11	0
C	58.14	-45.49	0	H	53.07	-14.95	0
C	56.98	-44.69	0	H	39.40	-9.05	0
C	57.12	-43.30	0	H	48.63	-13.28	0
C	58.38	-42.71	0	H	50.64	-14.68	0
C	59.55	-43.50	0	H	53.09	-11.13	0
C	63.69	-44.94	0	H	51.13	-9.75	0
C	62.03	-43.27	0	H	43.07	-6.03	0
C	64.31	-42.66	0	H	40.85	-7.08	0
C	66.72	-38.39	0	H	42.70	-10.97	0
C	66.60	-39.78	0	H	44.87	-9.96	0
C	65.34	-40.40	0	H	68.75	-23.04	0
C	64.19	-39.58	0	H	50.84	-6.42	0
C	64.31	-38.19	0	H	27.42	-13.61	0
C	65.58	-37.58	0	H	21.97	-37.49	0
C	65.73	-36.10	0	H	39.92	-54.15	0
C	65.78	-31.73	0	H	63.32	-46.93	0

Figure S5 shows the comparison of experimental and theoretical UV-Vis. spectrum for the PPDA-TFPT-COF. For the experimental spectrum $\lambda_{\text{on-set}}$ is calculated using the plot with a value of 390 nm. For the calculation of theoretical spectra, TD-DFT results are used. The TD-DFT plots show the ϵ vs. λ

plot which is calculated using the equation $\epsilon_i(v) = \epsilon_i^{\text{max}} \exp \left[-\left(\frac{v - v_i}{\sigma} \right)^2 \right]$ Eq.(S1)

where v is the excitation energy (in wavenumbers) corresponding to the electronic excitation, ϵ_i^{max} is the maximum of the band and σ is the standard deviation in wavenumbers. Although there is a significant difference in the UV-Vis spectra the $\lambda_{\text{on-set}}$ calculated using TD-DFT has the value of 401 nm which is quite close to the experimental results.

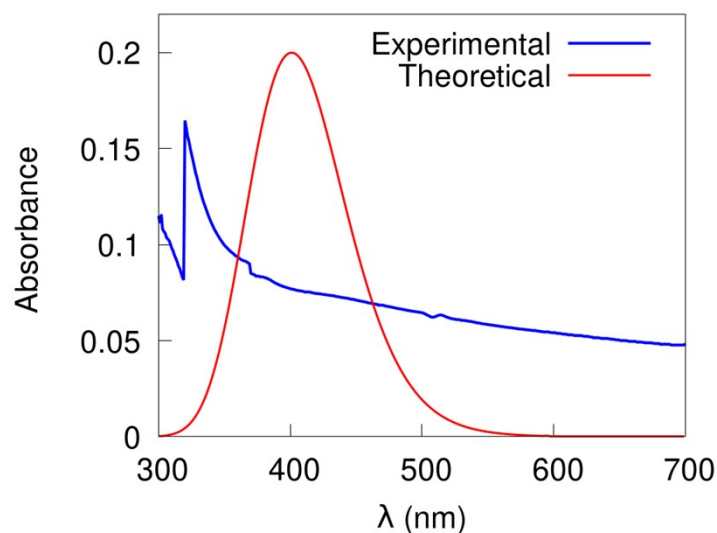


Figure S5: The comparison of the experimental and theoretical UV-Vis. spectrum. The experimental spectrum is calculated using solid-state UV-Vis. spectroscopy and the theoretical spectrum is calculated using TD-DFT calculations. TD-DFT results were scaled to compare them with the experimental spectrum and to visualize the λ_{\max} nicely.

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