

Electronic Supporting Information

Covalent Organic Framework based on BOPHY and hybrid thereof for solar fuels production

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1. General information

Materials. All the reagents including solvents were commercially available, unless otherwise noted, and used without further purification.

Nuclear magnetic resonance (NMR). Nuclear magnetic resonance (NMR) spectra were recorded with a Varian Mercury AS400 spectrometer (Larmor frequencies of 100 and 400 MHz for ^{13}C and ^1H , respectively) for liquids and a Bruker AVIII/HD spectrometer (Larmor frequencies of 400 and 100 MHz for ^{13}C and ^1H , respectively) for solids. 4-mm MAS (magic angle spinning) probes spinning at a rate of 8 kHz were used for ^{13}C solid-state MAS NMR. The ^{13}C CP-MAS spectra were obtained using a contact time of 3.0 ms and a relaxation time of 5 s. The number of scans used for the ^{13}C CP-MAS spectra was chosen such that the S/N is greater than or equal to 20.

High resolution mass spectra (HRMS) were recorded in an Agilent 6546LC Q-TOF instrument coupled with an ultra-high performance liquid chromatography (UHPLC) 1260 Infinity II model with an ESI source (ESI+ for **2**, and ESI- for **1**).

FTIR spectroscopy. Fourier Transform Infrared (FTIR) spectra were recorded on a Thermo-Scientific model Nicolet 6700 spectrometer and are reported in terms of the wavenumber of absorption (cm^{-1}).

X-ray diffraction. Powder X-ray diffraction (PXRD) patterns were collected at the X-ray diffraction facility of the Materials Science Institute of Madrid. Data was collected in transmission mode, with a Bruker D8 venture diffractometer, using Cu K α radiation ($\lambda = 1.54178$ Å). A glass capillary with 1.0 mm diameter was filled with the COF sample, and rotated while being irradiated for 300 s. Diffraction data was recorded with a Photon III detector, which was positioned at 125 mm distance from the sample. The recorded images were integrated with Bruker EVA software to generate the corresponding diffractogram.

Thermal Analysis. Thermo gravimetric analysis (TGA) was conducted in an argon or air stream with a TA Instruments Model TA-STD-Q600 analyzer. The samples were heated from 40 °C to 800 °C with a heating rate of 10 °C $\times$ min $^{-1}$.

Nitrogen sorption isotherm measurements. Porosity and surface area of the materials were characterized by nitrogen adsorption and desorption isotherms measurement at 87 K, using Micromeritics, TriStar II Plus. Prior to measurement, the samples were degassed for 12h at 100 °C. The surface area was determined by BET (Brunauer-Emmett-Teller) theory. The porous size was determined by using the non-local density functional theory (NLDFT) model.

Ultraviolet–visible spectroscopy (UV-Vis). The experiments were driven in a Perkin Elmer Lambda 1050 UV/Vis/NIR spectrometer. Solid samples were measured in terms of diffuse reflectance.

Cyclic voltammetry (CV). CV experiments were measured on a three-electrode electrochemical cell. The experiments were conducted in acetonitrile with tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. A dispersion of the IEC-2 was prepared by mixing 2 mg and 500 μL of isopropanol. The dispersion was deposited and dried on carbon paper and was used as working electrode. The counter electrode was a platinum wire, and an Ag wire electrode was used as a pseudo-reference (calibrated with ferrocene). Voltage and current density were measured with a potentiostat-galvanostat PGSTAT204. Current and voltage signals were

measured at a scan rate of 0.02 V s⁻¹ through an Autolab PGSTAT204 potentiostat/galvanostat station. The curves were calibrated with the ferrocene/ferrocenium (Fc/ Fc⁺) pair. The HOMO and LUMO energy levels of the COF were obtained according to the Equations (1) and (2):

$$E_{HOMO}(eV) = - [4.8 - \frac{E_1(Fc/Fc^+)}{2} + E_{ox,onset}] \quad (1)$$

$$E_{LUMO}(eV) = - [4.8 - \frac{E_1(Fc/Fc^+)}{2} + E_{red,onset}] \quad (2)$$

The half-wave potential of the Fc/Fc⁺ redox couple was estimated from Equation (3):

$$E_{1/2}(Fc/Fc^+) = (E_{ap} + E_{cp})/2 \quad (3)$$

Photonic efficiency (ζ). Photonic efficiency is the ratio between the rate of the photoreaction measured for a specified time interval to the rate of incident photons a defined wavelength interval, inside the irradiation window of the reactor¹.

In this work, the photonic efficiencies were calculated according to the Equation (4):

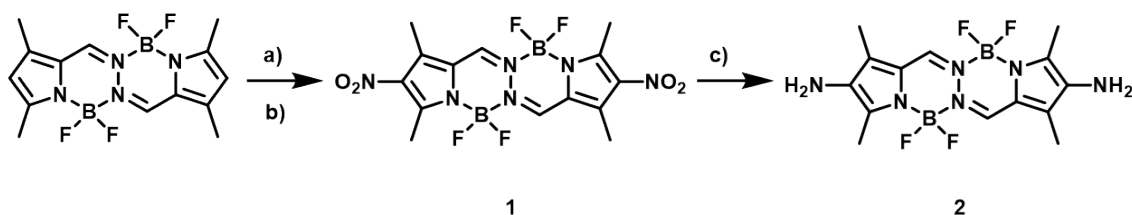
$$\zeta = \frac{\frac{dN}{dt}}{\int_{\lambda_1}^{\lambda_2} q_{p,\lambda}^0 dt} \quad (4)$$

where dN/dt represents the H₂ production rate, and $q_{p,\lambda}^0$ is the incident spectral photon flux within a defined wavelength range (eg. 250 – 400 nm). The incident spectral photon flux was calculated from the lamps emission spectra (see Figure S15), recorded with a StellarNet UVNb-50 radiometer connected to an optical fiber. The superscript 0 (zero) emphasizes that the incident number of photons (prior to absorption) is also considered. For solar H₂ evolution experiments, the incident solar radiation intensity was measured with a solar UV-A (300-400 nm) radiometer (ACADUS85-PLS), mounted on a platform sharing the same angle as the CPC. The number of incident photons has been estimated by applying the AM1.5 spectrum to the average irradiance obtained from the radiometer during the reaction.²

2. Synthetic Procedures and NMR Spectra

Synthesis of 2,7-diamino BOPHY building block

The synthesis of 2,7-diamino-BOPHY (**2**) used as building block to prepare the BOPHY-COF, **IEC-2**, consists of 2 steps (**Scheme S1**). The BOPHY chromophore uses as starting compound was synthesized following the experimental procedure described by Ziegler.³ After that, a first nitration step afforded the 2,7 dinitro-BOPHY (**1**). The second step consists in a reduction with Zn to achieve 2,7-diamino BOPHY monomer (**2**). Both BOPHY **1** and **2** have been reported for the first time in this work.



a) (Ac)₂O, HNO₃, -40 °C, 3h; b) r. t., 24h; c) HCOONH₄, Zn (dust), MeOH, r. t., Ar., 2,5h.

Scheme S1. Synthesis of BOPHY **2**

Synthesis of 2,7-dinitro-1,3,6,8-tetramethyl-bis(difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine (1): 1,3,6,8-tetramethyl-bis(difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine (100 mg, 0.3 mmol) and acetic anhydride (0.6 mL, 6.3 mmol) were placed in a round bottom flask. The mixture was stirred and brought to -40 °C with a liquid N₂ and chloroform bath, and 120 µL of nitric acid (65%) was added afterwards. The reaction was left at -40 °C for 3 h, the bath was removed and the mixture was stirred at room temperature for another 24 h. The mixture obtained was poured in an ice bath, the precipitate was filtered, washed with cold H₂O (250 mL) and dried under vacuum to obtain the compound **1** (90 mg, 70%) as a yellow solid. ¹H NMR (400 MHz, (CD₃)₂SO, 25 °C, TMS): δ=8.90 (s, 2H, H_a, H_{a'}), 2.78 (s, 6H, 3H_b, 3H_{b'}), 2.67 (s, 6H, 3H_c, 3H_{c'}) ppm. Solid-state ¹³C CP/MAS NMR (400 MHz) δ=150.8 (C_a, C_{a'}), 140.8 (C_b, C_{b'}), 139.3 (C_c, C_{c'}, C_d, C_{d'}), 120.1 (C_e, C_{e'}), 13.8 (C_f, C_{f'}), 10.0 (C_g, C_{g'}). MS (ESI-) m/z (%) = 427.1118 [M (nominal mass) -H]⁻ (100). HRMS MALDI: calculated for C₁₄H₁₄B₂F₄N₆O₄ 428.1199, found 428.1188.

Synthesis of 2,7-diamino-1,3,6,8-tetramethyl-bis(difluoroboron)-1,2-bis((1H-pyrrol-2-yl)methylene)hydrazine (2): HCO₂NH₄ (189.2 mg, 3 mmol) and Zn dust (189.2 mg, 3 mmol) were added to a solution of **1** (50 mg, 0.12 mmol) in MeOH (10 mL). The mixture was stirred for 2.5 h under argon atmosphere until the yellow solution turned red. The reaction mixture was filtered to eliminate the Zn, and the residue was purified by flash column chromatography (DCM/Methanol 9:1) to furnish **2** as a red solid (15 mg, 34%). ¹H NMR (400 MHz, (CD₃)₂SO, 25 °C, TMS): δ=7.78 (s, 2H, H_a, H_{a'}), 4.53 (s, 4H, 2H_b, 2H_{b'}), 2.33 (s, 6H, 3H_c, 3H_{c'}), 2.11 (s, 6H, 3H_d, 3H_{d'}) ppm. Solid ¹³C NMR (400 MHz) δ=140.1 (C_a, C_{a'}), 137.6 (C_b, C_{b'}), 130.4 (C_c, C_{c'}), 120.9 (C_d, C_{d'}), 118.7 (C_e, C_{e'}), 11.1 (C_f, C_{f'}), 7.7 (C_g, C_{g'}). MS (ESI+) m/z (%) = 369.1787 [M (nominal mass) +H]⁺ (100). HRMS MALDI: calculated for C₁₄H₁₈B₂F₄N₆ 368.1715, found 368.1717.

NMR Spectra

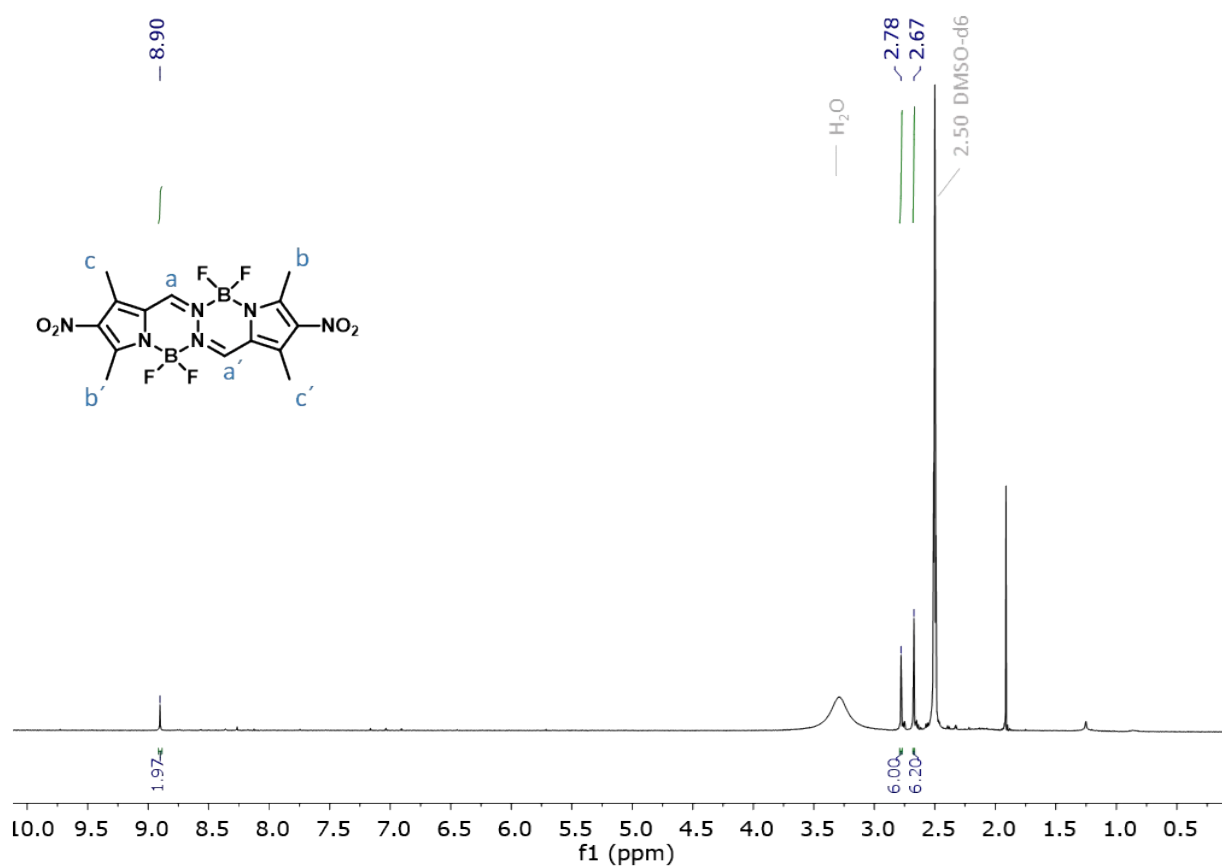


Figure S1. ¹H NMR spectra of compound 1.

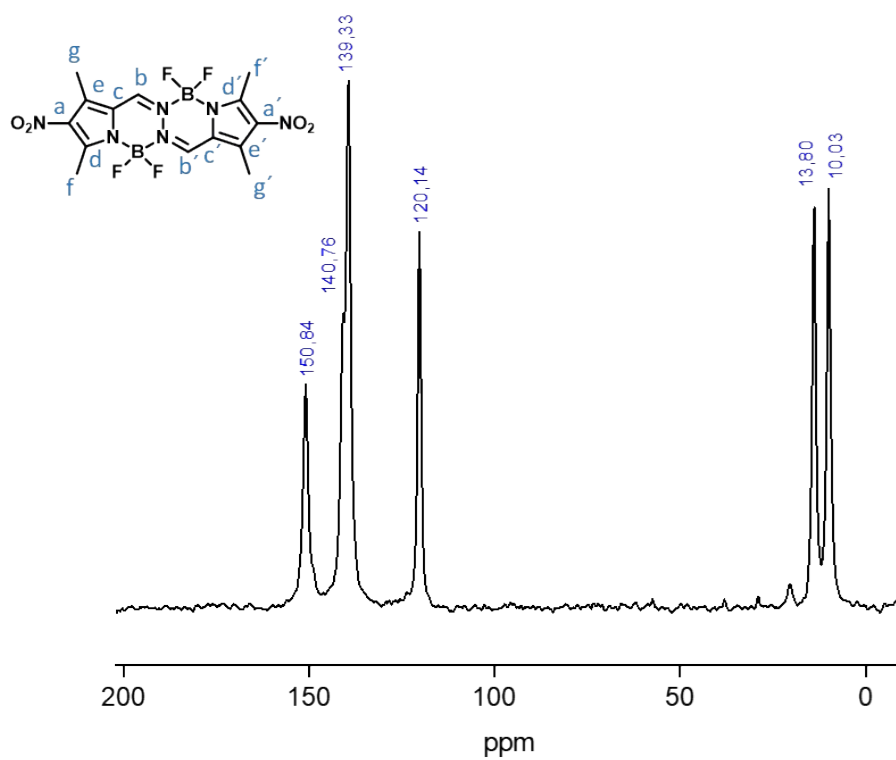


Figure S2. Solid ¹³C NMR spectra of compound 1.

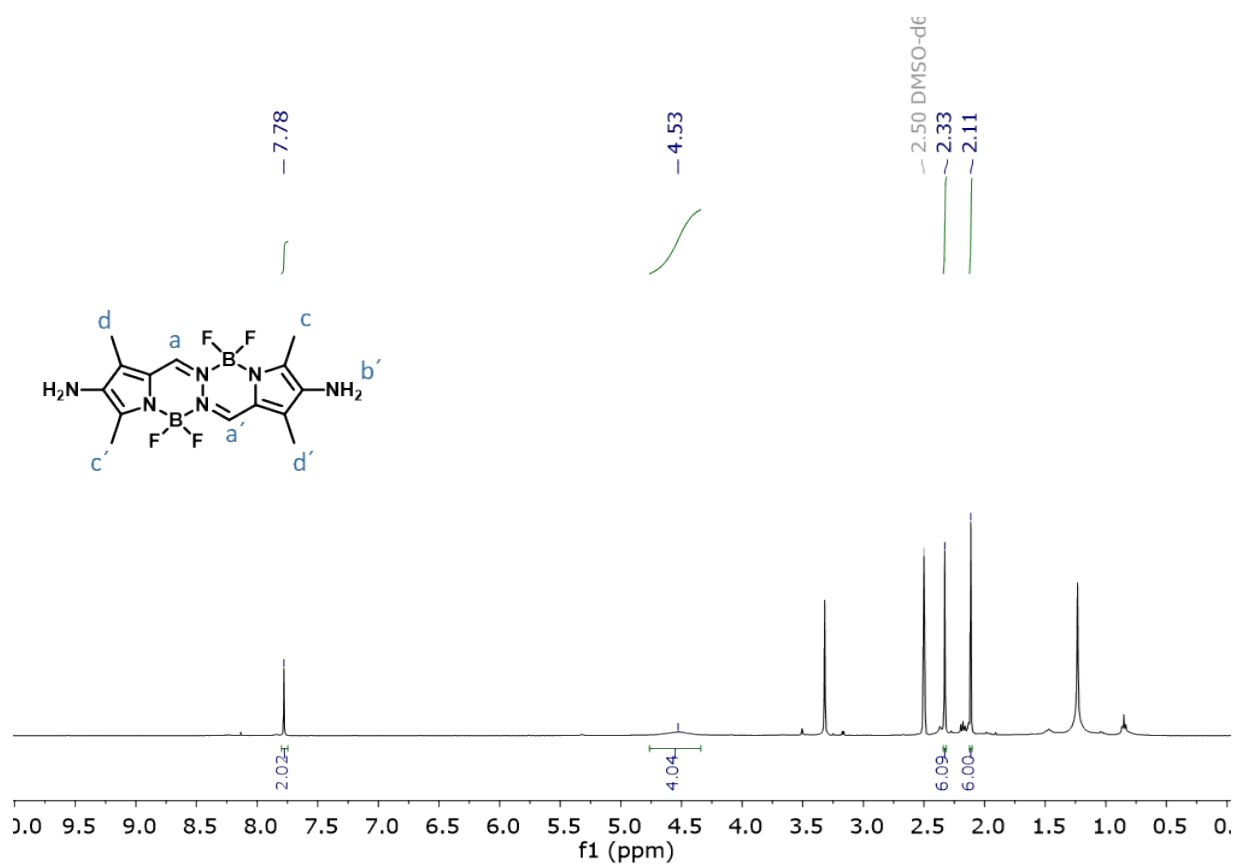


Figure S3. ¹H NMR spectra of compound 2.

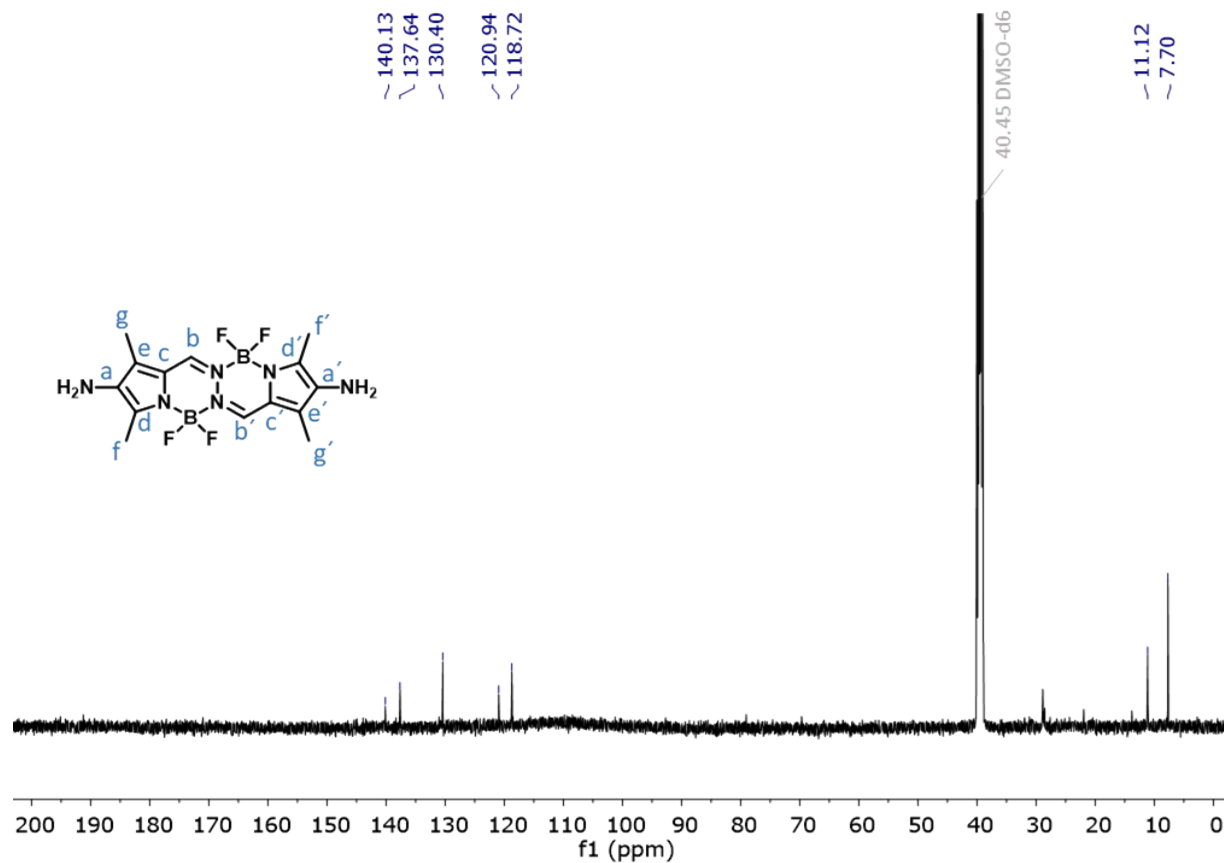


Figure S4. ¹³C NMR spectra of compound 2.

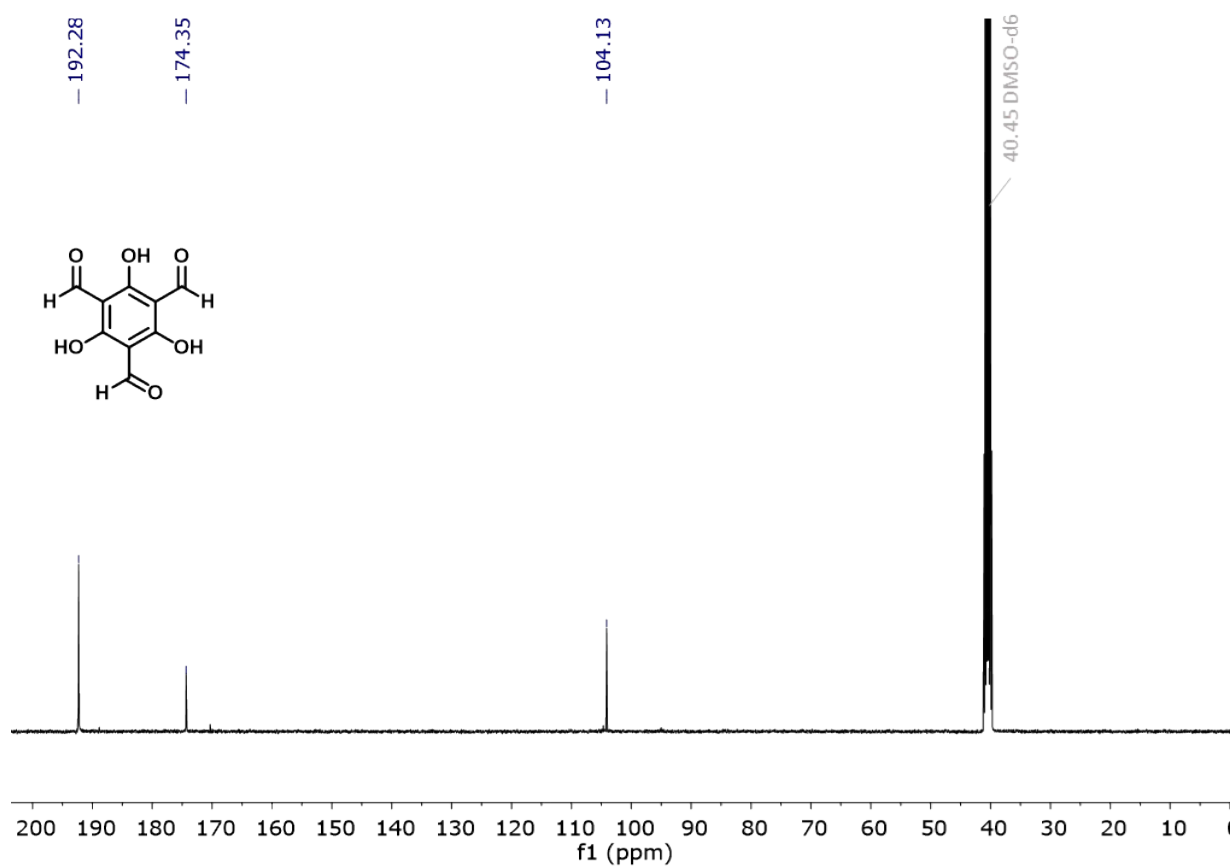


Figure S5. ^{13}C NMR spectra of 1,3,5-Triformylphloroglucinol **Tp**.

Synthesis of IEC-2.

The synthesis reported in the main text is the result of an optimization process of the operation conditions: the time and temperature of reaction was fixed to 4 days and 100°C, respectively but the mixture of solvents change (Table S1). The result is a compromise between the reaction yields (Table S1) and the better crystallinity and absence of peak from the precursors (Figure S6). Thus, the synthetic conditions selected were those described in entry IV Table S1.

Table S1. Conditions for the IEC-2 synthesis

Compound	Solvent Mixture	Yield (%)
I	1,4-Dioxane/mesitylene 3:1	66
II	BuOH /mesitylene 3:1	70
III	BuOH /mesitylene 5:1	99
IV	BuOH /mesitylene 1:1	97
V	BuOH /mesitylene 8:1	70

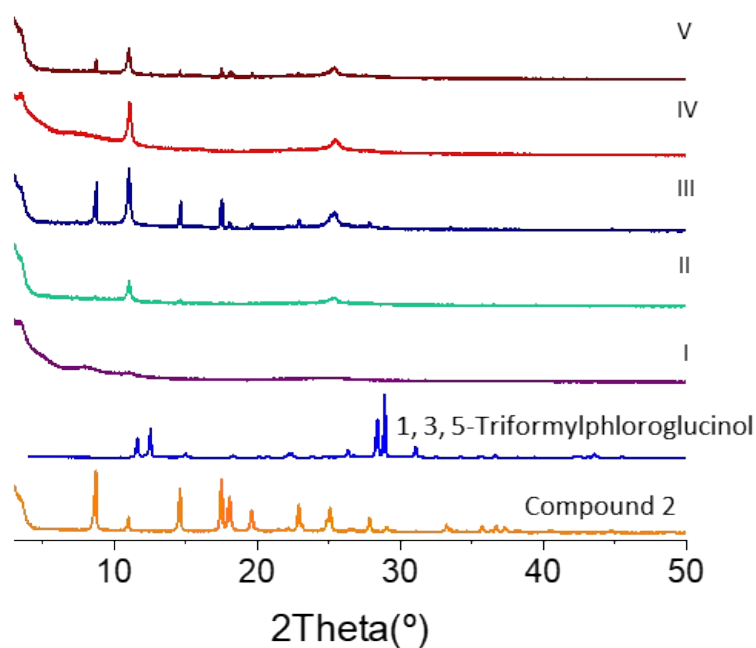


Figure S6. PXRD of IEC-2 as synthesized using different conditions (I to V, see Table S1) and PXRD of starting materials, **Tp** and **2**.

3. Structural analysis

Crystal structure models were built with the use of *Biovia Materials Studio 2022* software. The geometry of the BOPHY moieties was taken from RIXMAO CSD code crystal structure³. Models were geometrically optimized with energy minimization procedures, using the universal forcefield implemented in the Forcite module.

Atomic coordinate of IEC-2 model in CIF compatible format (copy in a text document to be read with any structure visualization software):

```
data_IEC-2
_audit_creation_date      2023-09-19
_audit_creation_method    'Materials Studio'
_symmetry_space_group_name_H-M  'CM'
_symmetry_Int_Tables_number  8
_symmetry_cell_setting    monoclinic
loop_
_symmetry_equiv_pos_as_xyz
  x,y,z
  x,-y,z
  x+1/2,y+1/2,z
  x+1/2,-y+1/2,z
_cell_length_a            33.6840
_cell_length_b            8.5600
_cell_length_c            28.8445
_cell_angle_alpha         90.0000
_cell_angle_beta          118.6149
_cell_angle_gamma         90.0000
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_adp_type
_atom_site_occupancy
H17  H   0.19097 0.10826 0.54031 0.00000 Uiso 1.00
H18  H   0.45529 0.10831 0.85575 0.00000 Uiso 1.00
H19  H   0.47811 0.10773 0.59225 0.00000 Uiso 1.00
H20  H   0.94972 0.10470 0.42338 0.00000 Uiso 1.00
H21  H   0.60385 0.10464 0.13176 0.00000 Uiso 1.00
H22  H   0.65068 0.10417 0.51179 0.00000 Uiso 1.00
H23  H   0.90721 0.10573 0.60559 0.00000 Uiso 1.00
H24  H   0.79505 0.10566 0.16364 0.00000 Uiso 1.00
H25  H   0.54498 0.10587 0.27412 0.00000 Uiso 1.00
H26  H   0.20599 -0.10475 0.75902 0.00000 Uiso 1.00
H27  H   0.61644 -0.10473 0.81544 0.00000 Uiso 1.00
H28  H   0.32987 -0.10497 0.35964 0.00000 Uiso 1.00
F1   F   0.57918 0.13360 0.50607 0.00000 Uiso 1.00
F2   F   1.02103 0.13483 0.48913 0.00000 Uiso 1.00
F3   F   0.58426 0.13546 0.04586 0.00000 Uiso 1.00
F4   F   0.40529 0.13522 0.34767 0.00000 Uiso 1.00
F5   F   0.11471 0.13504 0.70119 0.00000 Uiso 1.00
F6   F   0.66259 0.13467 0.92202 0.00000 Uiso 1.00
H1   H   0.28287 -0.00000 0.70979 0.00000 Uiso 1.00
```

H2	H	0.32606	-0.00000	0.48469	0.00000	Uiso	1.00
H3	H	0.69831	-0.00000	0.43805	0.00000	Uiso	1.00
H4	H	0.68766	-0.00000	0.23341	0.00000	Uiso	1.00
H5	H	0.62106	-0.00000	0.32412	0.00000	Uiso	1.00
H6	H	0.77815	-0.00000	0.23857	0.00000	Uiso	1.00
H7	H	0.48416	-0.00000	0.91437	0.00000	Uiso	1.00
H8	H	0.14056	-0.00000	0.51309	0.00000	Uiso	1.00
H9	H	0.62452	-0.00000	0.18828	0.00000	Uiso	1.00
H10	H	0.90196	-0.00000	0.39059	0.00000	Uiso	1.00
H11	H	0.57162	-0.00000	0.76156	0.00000	Uiso	1.00
H12	H	0.25437	-0.00000	0.76392	0.00000	Uiso	1.00
H13	H	0.78002	-0.00000	0.10336	0.00000	Uiso	1.00
H14	H	0.95772	-0.00000	0.64940	0.00000	Uiso	1.00
H15	H	0.41693	-0.00000	0.57798	0.00000	Uiso	1.00
H16	H	0.43063	-0.00000	0.78030	0.00000	Uiso	1.00
H29	H	0.25385	-0.00000	0.59108	0.00000	Uiso	1.00
H30	H	0.49780	-0.00000	0.27141	0.00000	Uiso	1.00
H31	H	0.30711	-0.00000	0.39630	0.00000	Uiso	1.00
H32	H	0.68744	-0.00000	0.49752	0.00000	Uiso	1.00
H33	H	0.51447	-0.00000	0.57761	0.00000	Uiso	1.00
H34	H	0.84941	-0.00000	0.51305	0.00000	Uiso	1.00
H35	H	0.85874	-0.00000	0.41450	0.00000	Uiso	1.00
H36	H	0.50058	-0.00000	0.73944	0.00000	Uiso	1.00
B1	B	0.11120	-0.00000	0.67133	0.00000	Uiso	1.00
B2	B	0.42523	-0.00000	0.37791	0.00000	Uiso	1.00
B3	B	1.02241	-0.00000	0.51780	0.00000	Uiso	1.00
B4	B	0.55977	-0.00000	0.47431	0.00000	Uiso	1.00
B5	B	0.60717	-0.00000	0.04294	0.00000	Uiso	1.00
B6	B	0.64216	-0.00000	0.92947	0.00000	Uiso	1.00
C1	C	0.09764	-0.00000	0.56252	0.00000	Uiso	1.00
C2	C	0.49898	-0.00000	0.48757	0.00000	Uiso	1.00
C3	C	1.02816	-0.00000	0.62346	0.00000	Uiso	1.00
C4	C	0.48930	-0.00000	0.36105	0.00000	Uiso	1.00
C5	C	0.47925	-0.00000	0.57128	0.00000	Uiso	1.00
C6	C	0.47544	-0.00000	0.87205	0.00000	Uiso	1.00
C7	C	0.33366	-0.00000	0.38412	0.00000	Uiso	1.00
C8	C	0.59427	-0.00000	0.80466	0.00000	Uiso	1.00
C9	C	0.53520	-0.00000	0.28859	0.00000	Uiso	1.00
C10	C	0.77760	-0.00000	0.14043	0.00000	Uiso	1.00
C11	C	0.65276	-0.00000	0.49023	0.00000	Uiso	1.00
C12	C	0.62480	-0.00000	0.15041	0.00000	Uiso	1.00
C13	C	0.41151	-0.00000	0.65524	0.00000	Uiso	1.00
C14	C	0.35933	-0.00000	0.69427	0.00000	Uiso	1.00
C15	C	0.37251	-0.00000	0.60091	0.00000	Uiso	1.00
C16	C	0.40566	-0.00000	0.70165	0.00000	Uiso	1.00
C17	C	0.38388	-0.00000	0.56284	0.00000	Uiso	1.00
C18	C	0.44049	-0.00000	0.75080	0.00000	Uiso	1.00
C19	C	0.44091	-0.00000	0.51279	0.00000	Uiso	1.00
C20	C	0.51675	-0.00000	0.86350	0.00000	Uiso	1.00
C21	C	0.39217	-0.00000	0.48448	0.00000	Uiso	1.00
C22	C	0.52279	-0.00000	0.81915	0.00000	Uiso	1.00
C23	C	0.38009	-0.00000	0.43054	0.00000	Uiso	1.00
C24	C	0.56983	-0.00000	0.83655	0.00000	Uiso	1.00
C25	C	0.45277	-0.00000	0.47482	0.00000	Uiso	1.00
C26	C	0.55934	-0.00000	0.90364	0.00000	Uiso	1.00
C27	C	0.55857	-0.00000	0.34817	0.00000	Uiso	1.00
C28	C	0.72917	-0.00000	0.12912	0.00000	Uiso	1.00

C29	C	0.53834	-0.00000	0.37910	0.00000	Uiso	1.00
C30	C	0.69101	-0.00000	0.08012	0.00000	Uiso	1.00
C31	C	0.61145	-0.00000	0.43518	0.00000	Uiso	1.00
C32	C	0.66487	-0.00000	0.13743	0.00000	Uiso	1.00
C33	C	0.60492	-0.00000	0.38330	0.00000	Uiso	1.00
C34	C	0.71348	-0.00000	0.16617	0.00000	Uiso	1.00
C35	C	0.79668	-0.00000	0.40107	0.00000	Uiso	1.00
C36	C	0.71457	-0.00000	0.37940	0.00000	Uiso	1.00
C37	C	0.68459	-0.00000	0.39706	0.00000	Uiso	1.00
C38	C	0.72120	-0.00000	0.25395	0.00000	Uiso	1.00
C39	C	0.76269	-0.00000	0.41871	0.00000	Uiso	1.00
C40	C	0.70207	-0.00000	0.32318	0.00000	Uiso	1.00
C41	C	0.78331	-0.00000	0.34400	0.00000	Uiso	1.00
C42	C	0.84033	-0.00000	0.43338	0.00000	Uiso	1.00
C43	C	0.73649	-0.00000	0.30558	0.00000	Uiso	1.00
C44	C	0.91297	-0.00000	0.51228	0.00000	Uiso	1.00
C45	C	0.94046	-0.00000	0.48678	0.00000	Uiso	1.00
C46	C	0.98458	-0.00000	0.57356	0.00000	Uiso	1.00
C47	C	0.94139	-0.00000	0.56687	0.00000	Uiso	1.00
C48	C	0.14110	-0.00000	0.60651	0.00000	Uiso	1.00
C49	C	0.19419	-0.00000	0.68639	0.00000	Uiso	1.00
C50	C	0.21385	-0.00000	0.65282	0.00000	Uiso	1.00
C51	C	0.17848	-0.00000	0.60073	0.00000	Uiso	1.00
C52	C	0.27724	-0.00000	0.63134	0.00000	Uiso	1.00
C53	C	0.31988	-0.00000	0.64058	0.00000	Uiso	1.00
C54	C	0.32707	-0.00000	0.59341	0.00000	Uiso	1.00
C55	C	0.93302	-0.00000	0.42881	0.00000	Uiso	1.00
C56	C	0.92770	-0.00000	0.60942	0.00000	Uiso	1.00
C57	C	0.21709	-0.00000	0.74552	0.00000	Uiso	1.00
C58	C	0.17574	-0.00000	0.54626	0.00000	Uiso	1.00
C59	C	0.68759	-0.00000	0.02656	0.00000	Uiso	1.00
C60	C	0.56794	-0.00000	0.95591	0.00000	Uiso	1.00
N1	N	1.06545	-0.00000	0.62030	0.00000	Uiso	1.00
N2	N	0.47634	-0.00000	0.39653	0.00000	Uiso	1.00
N3	N	0.06339	-0.00000	0.56955	0.00000	Uiso	1.00
N4	N	0.50951	-0.00000	0.45134	0.00000	Uiso	1.00
N5	N	0.36140	-0.00000	0.50692	0.00000	Uiso	1.00
N6	N	0.48799	-0.00000	0.76573	0.00000	Uiso	1.00
N7	N	0.41801	-0.00000	0.42587	0.00000	Uiso	1.00
N8	N	0.59177	-0.00000	0.88944	0.00000	Uiso	1.00
N9	N	0.57007	-0.00000	0.43026	0.00000	Uiso	1.00
N10	N	0.65407	-0.00000	0.08662	0.00000	Uiso	1.00
N11	N	0.63679	-0.00000	0.36477	0.00000	Uiso	1.00
N12	N	0.74294	-0.00000	0.22254	0.00000	Uiso	1.00
N13	N	0.86479	-0.00000	0.48903	0.00000	Uiso	1.00
N14	N	0.98276	-0.00000	0.52605	0.00000	Uiso	1.00
N15	N	0.14904	-0.00000	0.65661	0.00000	Uiso	1.00
N16	N	0.26121	-0.00000	0.66936	0.00000	Uiso	1.00
N17	N	0.60825	-0.00000	0.99285	0.00000	Uiso	1.00
N18	N	0.64735	-0.00000	-0.01453	0.00000	Uiso	1.00
O1	O	0.77387	-0.00000	0.46570	0.00000	Uiso	1.00
O2	O	0.66255	-0.00000	0.28939	0.00000	Uiso	1.00
O3	O	0.35433	-0.00000	0.73340	0.00000	Uiso	1.00
O4	O	0.29523	-0.00000	0.54857	0.00000	Uiso	1.00
O5	O	0.44964	-0.00000	0.66060	0.00000	Uiso	1.00
O6	O	0.81180	-0.00000	0.32928	0.00000	Uiso	1.00
END							

4. Gas Sorption Studies

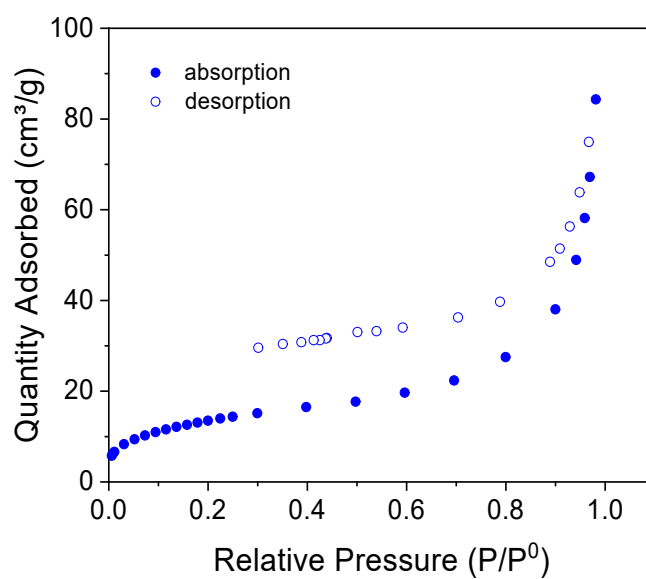


Figure S7. N_2 adsorption and desorption isotherm of IEC-2.

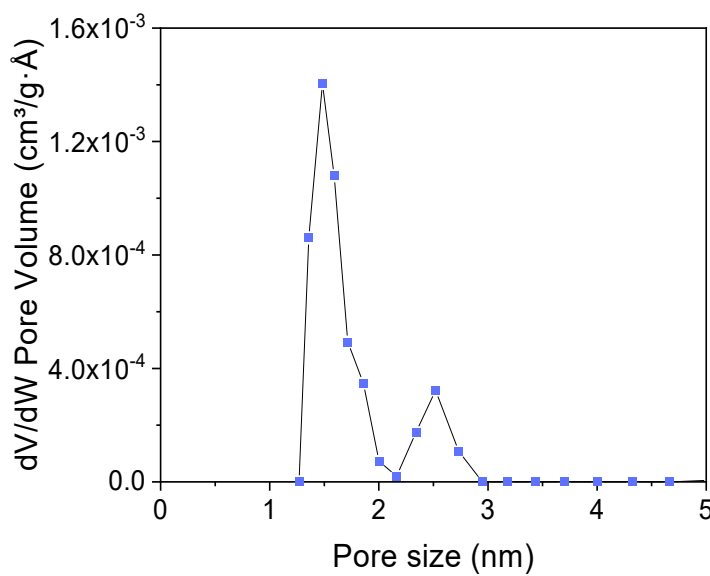


Figure S8. Pore size distribution of IEC-2 calculated with non-local density functional theory (NLDFT).

5. Thermogravimetric Analysis

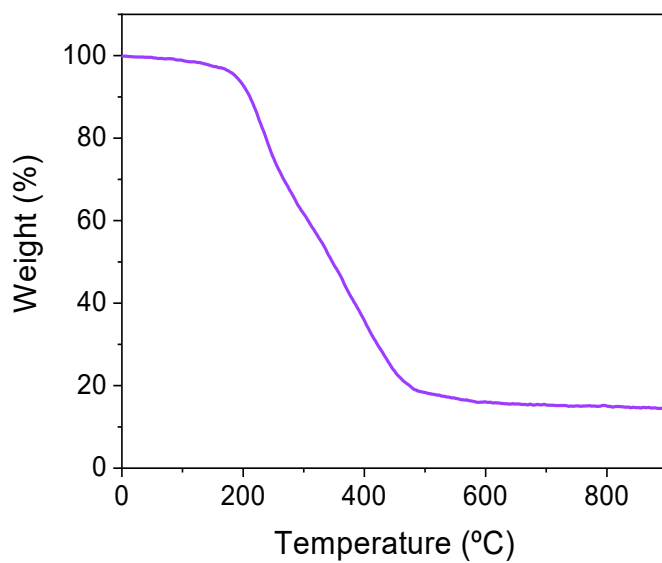


Figure S9. TGA data of activated **IEC-2** under air atmosphere.

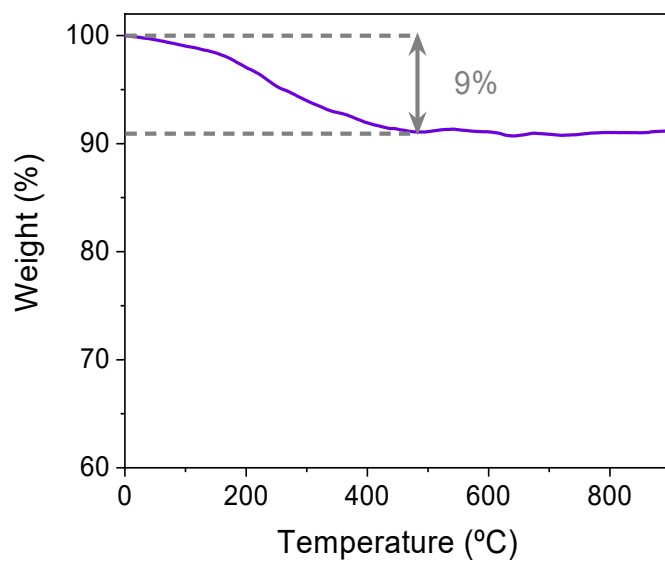


Figure S10. TGA data of activated **IEC-2@T-10** under air atmosphere.

6. CV measurements

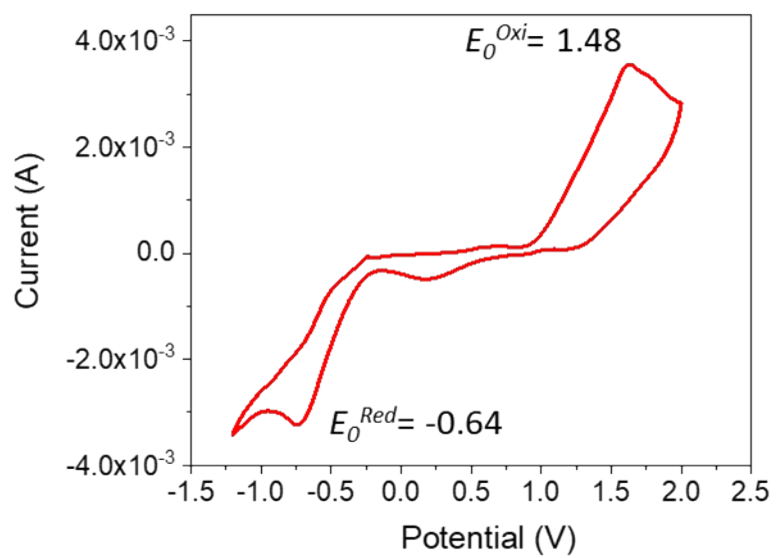


Figure S11. Cyclic voltammetry (CV) of **IEC-2** measured using as electrolyte 0.1M of TBA perchlorate in acetonitrile at a scan rate of 20 mV s^{-1} .

7. Diffuse Reflectance

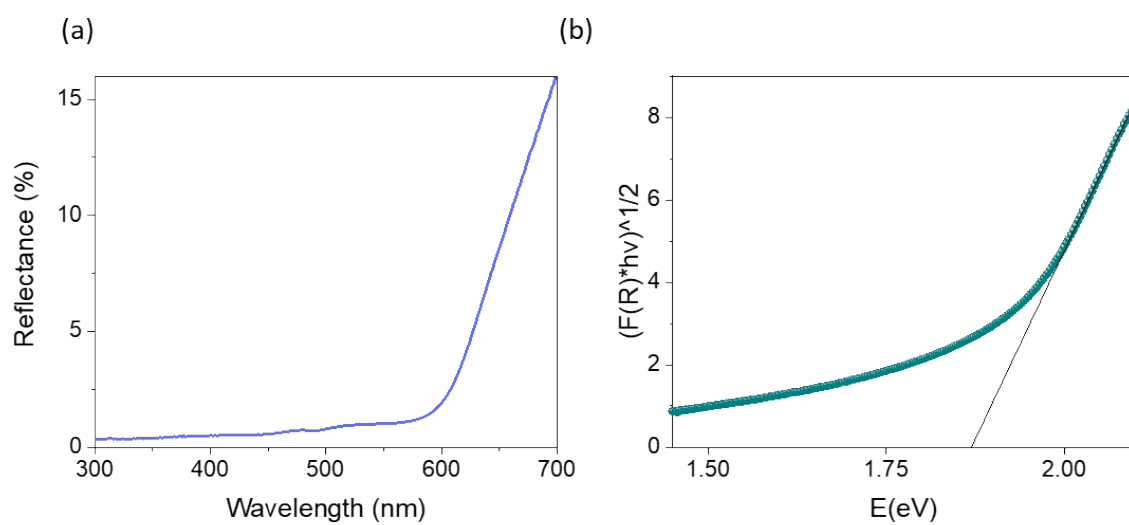


Figure S12. (a) Diffuse reflectance of IEC-2 (b) Tauc plots as indirect transition of IEC-2.

8. Emission spectrum of Hg-lamp used in the lab scale photocatalytic tests

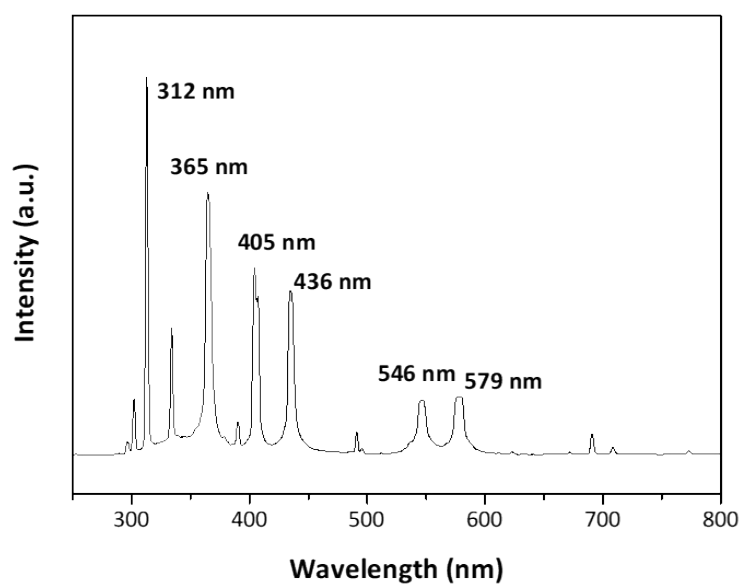


Figure S13. Spectrum of the Hg-lamp used in the photocatalytic experiments.

9. Photocatalytic Hydrogen Evolution Experiments

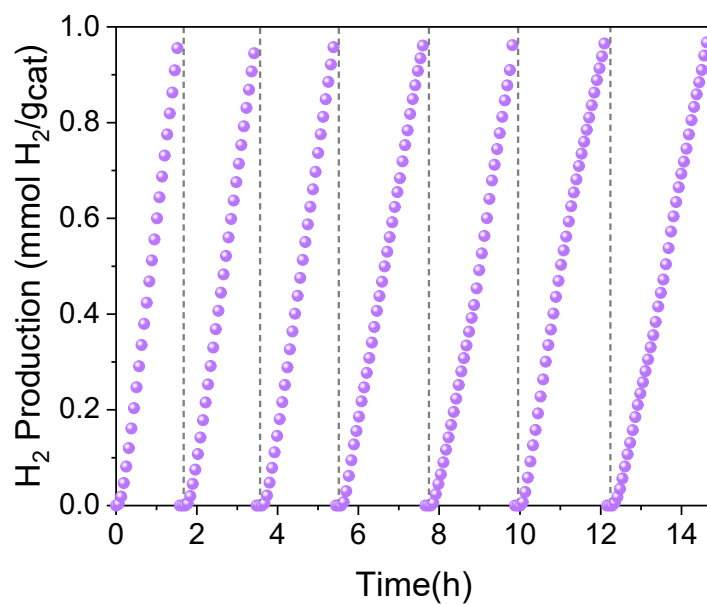


Figure S14. Recyclability of IEC-2@T-10 for H₂ production using UV-dark cycles.

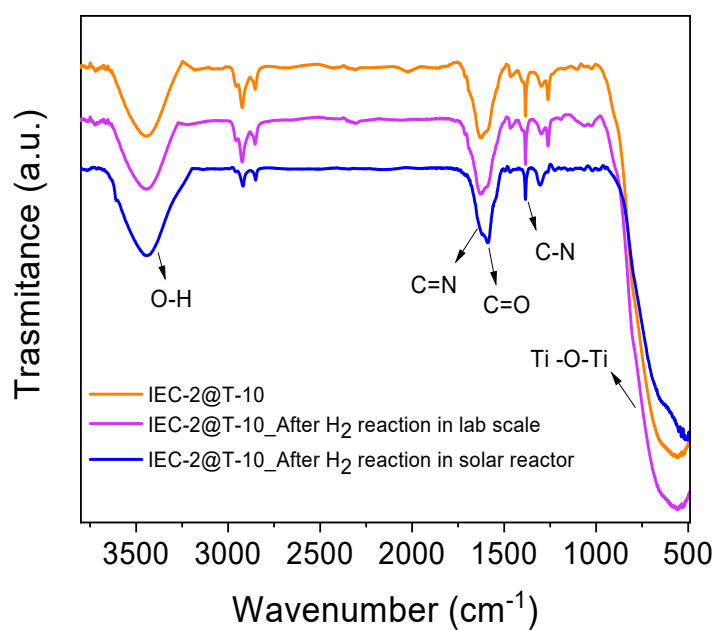


Figure S15. FTIR spectra of IEC-2@T-10 before and after H₂ evolution reaction tests.

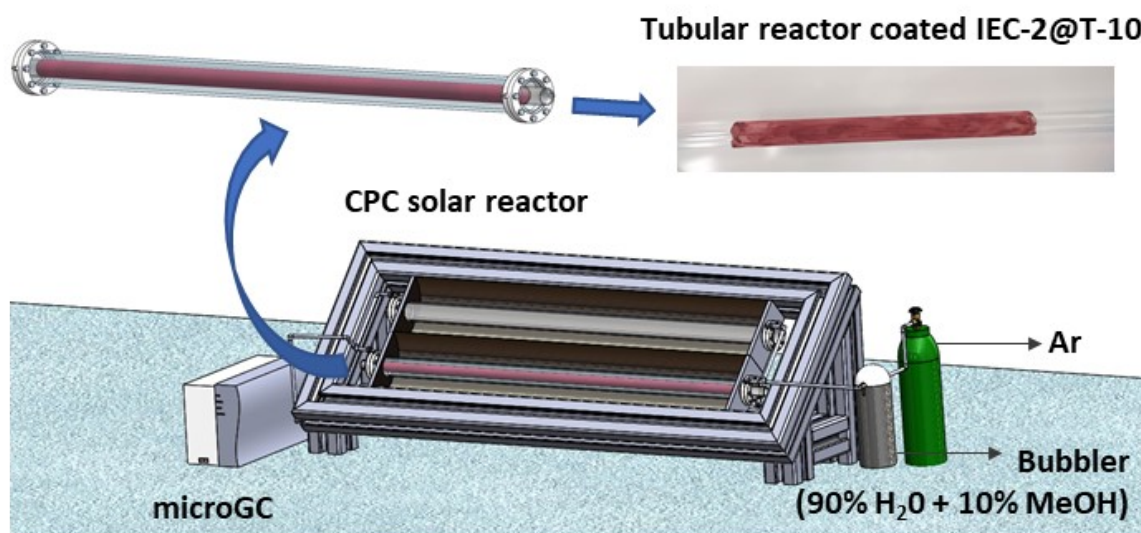


Figure S16. Schematic assembly of the semi-pilot plant scale CPC photoreactor.

10. Charge transfer mechanism elucidation

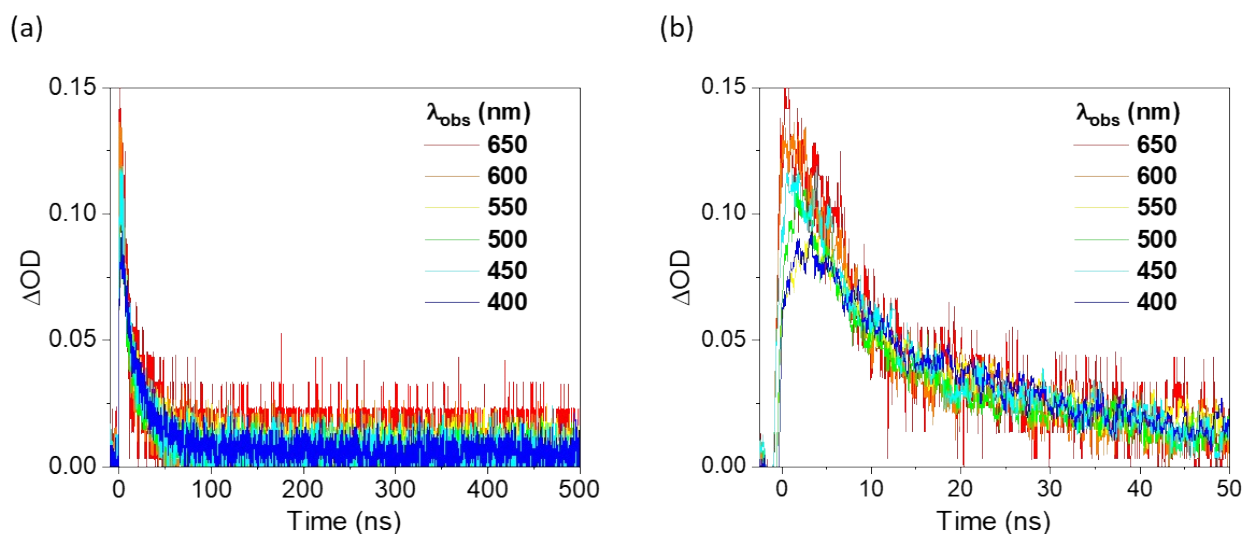


Figure S17 A) Transient decay traces ($\lambda_{exc} = 355$ nm) for the polymer IEC-2 at different wavelengths of acquisition (from 400 to 650 nm). Note that the maximum of TA in terms of DOD correspond to the traces at 400-450 nm. All the samples were measured in 10 vol% aqueous methanol suspension under N_2 . B) Zoom image for the first 50 ns after laser pulse.

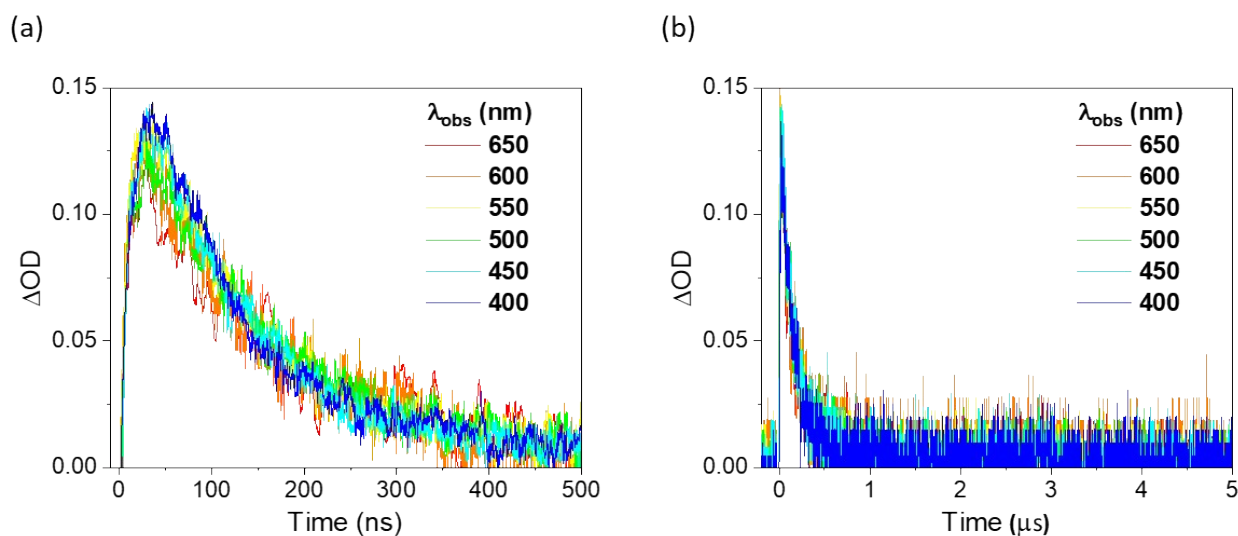


Figure S18. Transient decay traces ($\lambda_{exc} = 355$ nm) for the hybrid IEC-2@T-10 at different wavelengths of acquisition (from 400 to 650 nm). All the samples were measured in 10 vol% aqueous methanol suspension under N_2 monitored up to 500 ns (A) or 5 μs (B) after laser pulse. Note that the maximum of TA in terms of DOD correspond to the traces at 600-650 nm.

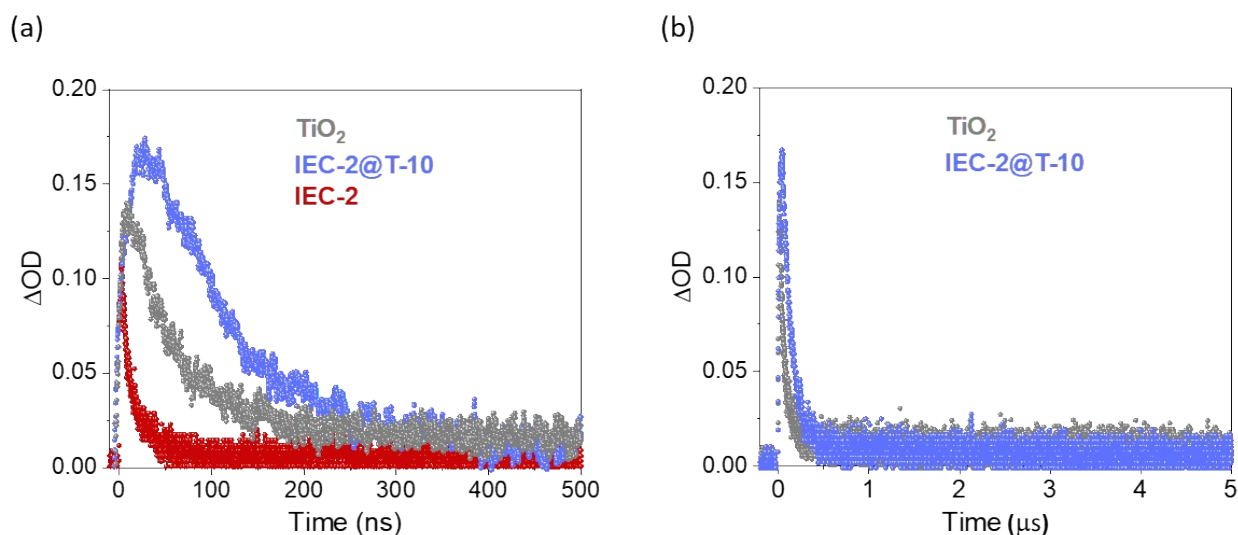


Figure S19 Transient decay traces ($\lambda_{\text{exc}} = 355 \text{ nm}$, $\lambda_{\text{obs}} = 460 \text{ nm}$) for TiO_2 (grey), the hybrid IEC-2@T-10 (purple) and the polymer IEC-2 (pink) measured up to 500 ns (A) or 5 μs (B) after laser pulse. All the samples were measured in 10 vol% aqueous methanol suspension under N_2 .

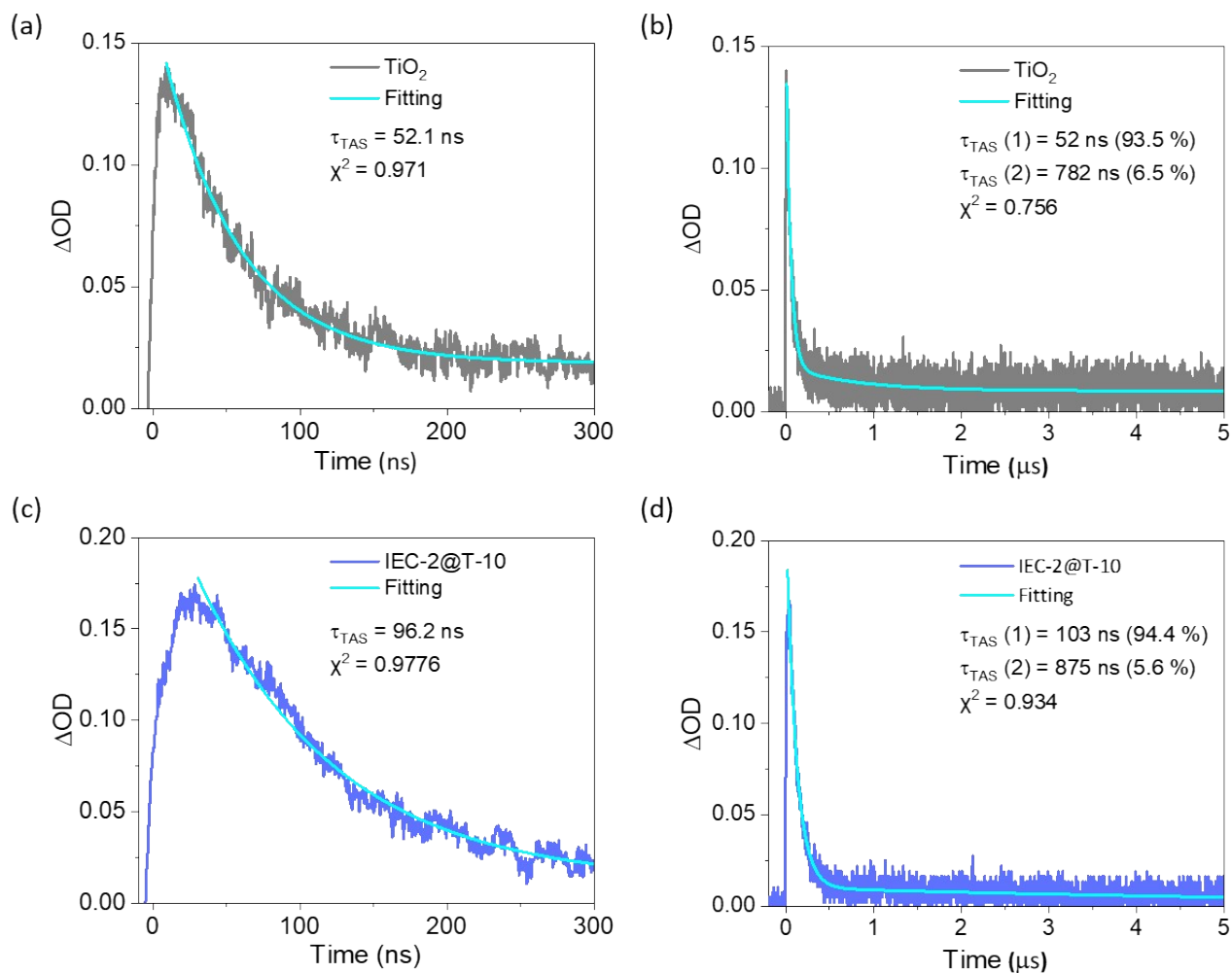


Figure S20 Fits of the transient decay traces ($\lambda_{\text{exc}} = 355 \text{ nm}$, $\lambda_{\text{obs}} = 460 \text{ nm}$) monitored up to 300 ns after laser pulse as mono-exponential functions (A and C) or until 5 μs as bi-exponential functions (B and D) for TiO_2 (A and B) and IEC-2@T-10 (C and D). All the measurements were registered in deaerated 10 vol% aqueous methanol suspensions under N_2 .

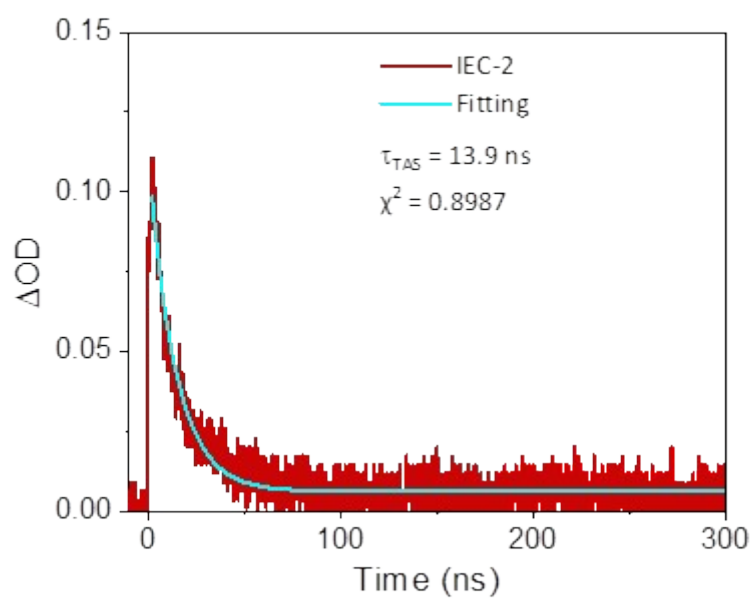


Figure S21 Transient decay trace ($\lambda_{\text{exc}} = 355 \text{ nm}$, $\lambda_{\text{obs}} = 460 \text{ nm}$) for the polymer **IEC-2** measured in 10 vol% aqueous methanol suspension under N_2 . The fitting curve (cyan) has been included.

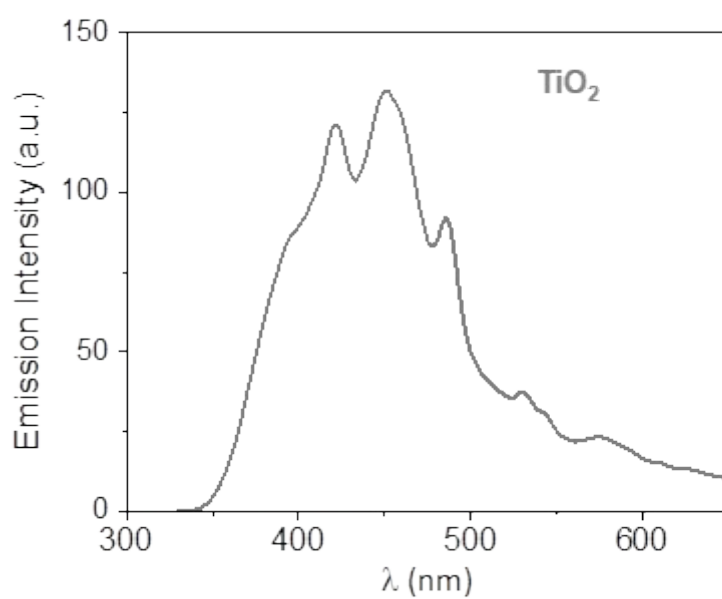


Figure S22 Photoluminescence spectrum ($\lambda_{\text{exc}} = 300 \text{ nm}$, cut-off filter at 350 nm) for TiO_2 measured in solid state.

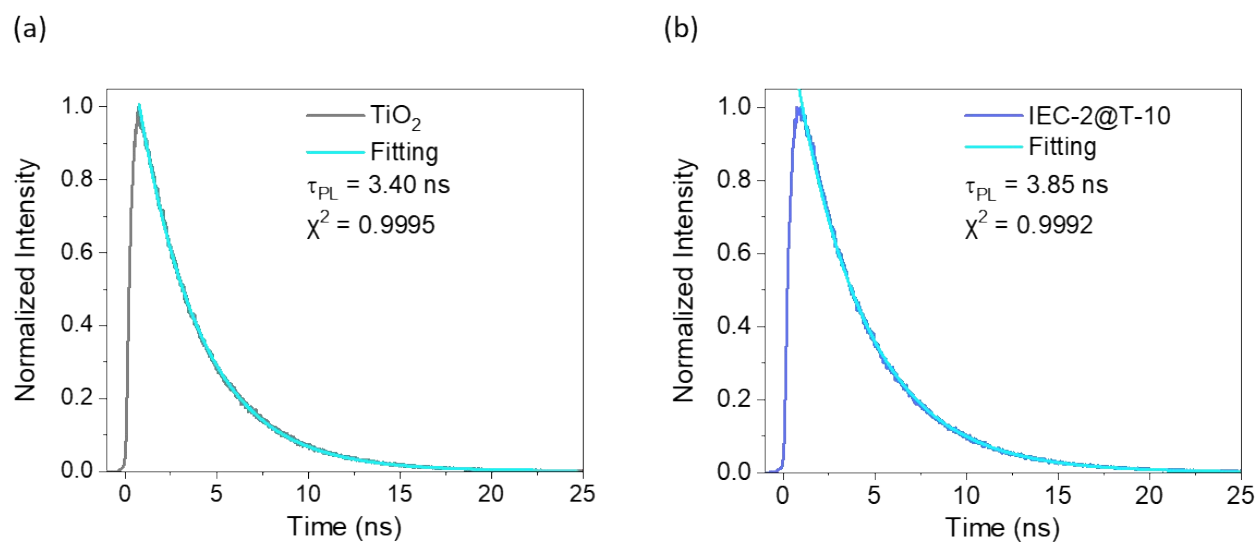


Figure S23 Normalized photoluminescence decay traces ($\lambda_{\text{exc}} = 372 \text{ nm}$, band-pass filter centered at 450 nm) for TiO_2 (A) and the hybrid **IEC-2@T-10** (B) measured in solid state. The fitting curves (cyan) have been included in all cases.

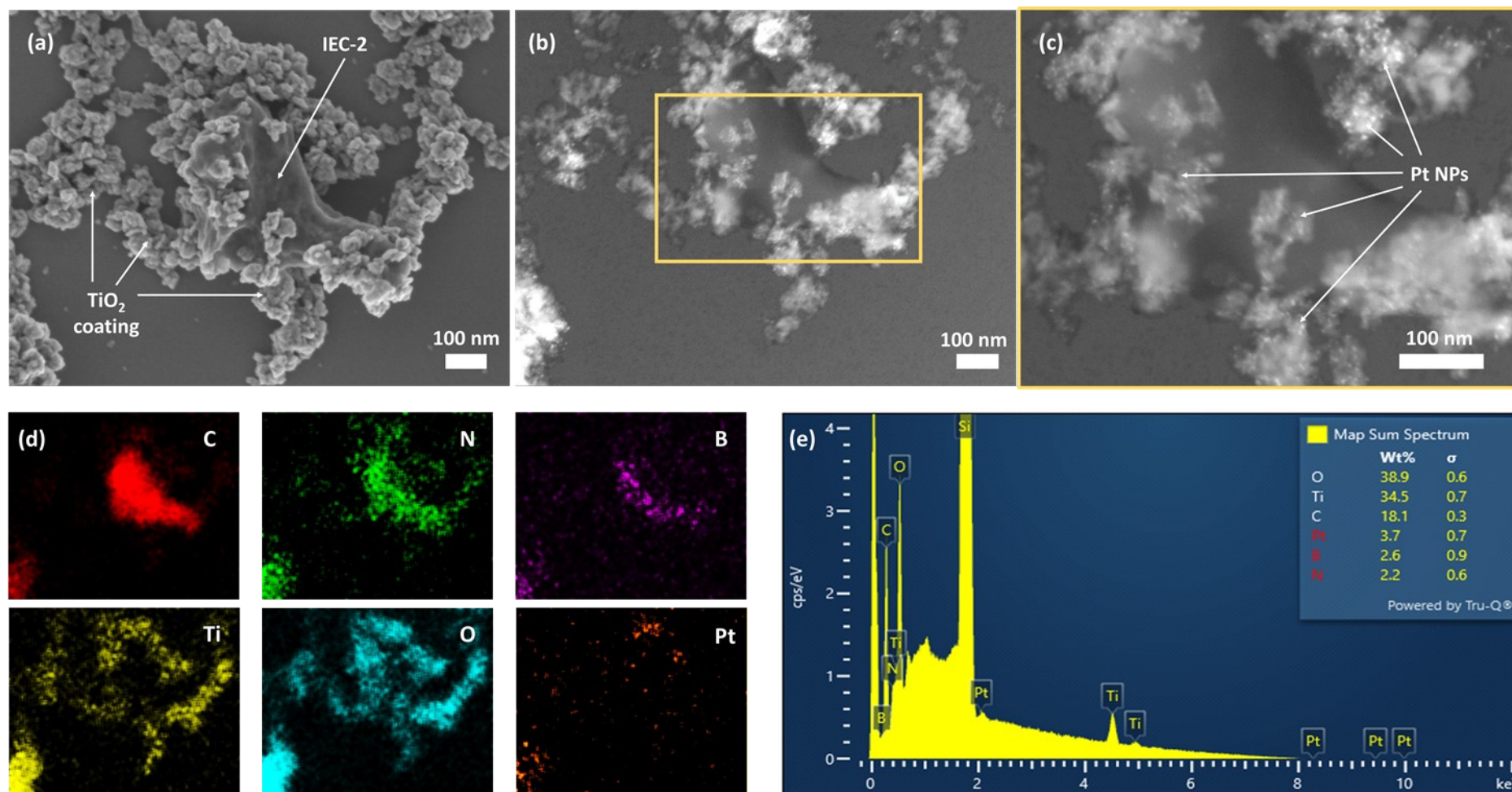


Figure S24. FESEM of Pt-3/IEC-2@T-10 sample: (a) High-resolution SEM image. (b) same as A taken with BED detector. (c) magnification of B. The brilliant spots on the TiO₂, are the metal nanoparticles. (d) X-EDS microanalysis images of image B showing Carbon (red), Nitrogen (green), Boron (purple) Titanium (yellow), Oxygen (blue), and Platinum (orange). (e) EDS spectrum from region B showing the presence of Platinum.

11. References

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- 2 P. García-Muñoz, J. Ivanez, V. A. de la Peña O'Shea, N. Keller and F. Fresno, *Catal. Today*, 2023, **413–415**, 0–6.
- 3 I.-S. Tamgho, A. Hasheminasab, J. T. Engle, V. N. Nemykin and C. J. Ziegler, *J. Am. Chem. Soc.*, 2014, **136**, 5623–5626.