Electronic Supplementary Information for

# Hydrogen-bonded organic framework based on redox-active tri(dithiolylidene)cyclohexanetrione

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## 1. General methods.

All the chemicals used as starting materials, reagents and solvents were purchased from commercial suppliers and used as received without further purification. Analytical thin layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel (Kieselgel $60F_{254}$, Merck). Column chromatographic purifications were performed using silica gel (63-200 μm, Merck and 64-210 μm, Wakosil®). Unless stated otherwise, reported yields refer to analytically pure samples. NMR spectra were recorded in $CDCl_3$ on AV 400 MHz JEOL ECX-400 NMR spectrometers. Chemical shifts are reported in δ ppm relative to solvent peak ($^1$H NMR: δ 7.26 ppm and 2.50 ppm for $CDCl_3$ and DMSO-$d_6$, respectively; $^{13}$C NMR: δ 77.16 ppm and 39.52 ppm for $CDCl_3$ and DMSO-$d_6$, respectively)[S1] with peak multiplicities described as singlet (s), broad singlet (br. s), doublet (d), triplet (t), quartet (q) and multiplet (m) in $^1$H NMR spectra. IR spectra were recorded using Thermo Scientific Nicolet 6700 FT-IR spectrometer in KBr tablets. Melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. High-resolution mass spectrometry (HRMS) measurements were performed using JEOL JMS-T100LP and Thermo Scientific Exactive mass spectrometers with ESI and APCI ionization methods. UV/vis spectrum was recorded on a Hitachi U-2910 and on a JASCO-V770 spectrophotometers for a solution and solid, respecitively. Fluorescence and excitation spectra were measured on a Hitachi F-7000 spectrofluorometer. Fluorescence quantum yields were determined by using 9,10-diphenylanthracene ($\Phi_F = 0.97$) as an external standard.[S2] Differential pulse voltammetry was conducted on a BAS ALS-600A in dry $CH_2Cl_2$ containing 0.1 M $Bu_4NBF_4$ as a supporting electrolyte. Pt electrodes were used as the working and counter electrodes. The working disk electrode was polished using a water suspension of aluminum oxide (0.05 μmol) before use. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima IV X-ray diffractometer (40 kV, 40 mA) using graphite-monochromatized Cu-Kα radiation (λ = 1.54187 Å) at room temperature. Thermogravimetric analysis was conducted using a Rigaku Thermo Plus TG8120 with a heating rate of 5 K/min under nitrogen. Gas sorption measurements on activated HOF **CPDC-1** were performed on BELSORP-max (BEL, Japan).

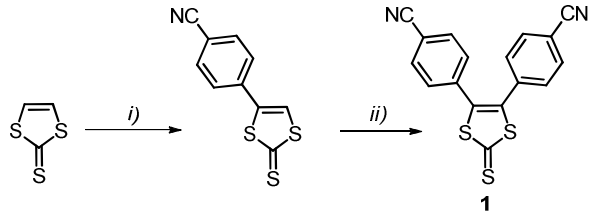
**Crystal Structure Determination.** Single crystalline X-ray diffraction data was collected by Rigaku MicroMax-007HF diffractometer with a Pilatus 200K detector and $Cu_{K\alpha}$ radiation (λ = 1.54184 Å) at 100K. Analytical and multi-scan absorption corrections were applied to the reflection data. A single crystal was mounted on MicroMounts™ tip (MiTeGen) with Paratone® 8277 (Hampton Research). Data collection, cell refinement, and data reduction were

carried out with Crysalis $^{PRO}$ (Rigaku Oxford Diffraction, 2017). The initial structure was solved by using SHELXT,[S3] and structural refinement was performed by using full-matrix least-squares techniques on $F^2$ using Crystal structure software (Rigaku). Anisotropic refinement was applied to all atoms except for hydrogens. SQUEEZE function equipped in the PLATON program was used to remove severely disordered solvent molecules in voids. These data are provided free of charge in The Cambridge Crystallographic Data Centre (CCDC-2038905).

**Photocurrent measurement.** FP-TRMC was performed for the powder samples placed on an adhesive tape on a quartz substrate. The microwave frequency and its power were ~9 GHz and ~3 mW, respectively. The third harmonic generation (355 nm) of a Nd:YAG laser (Continuum Inc., Surelite II, 5−8 ns pulse duration, 10 Hz) was used for the excitation (incident photon density $I_0 = 9.1 \times 10^{15}$ photons cm$^{-2}$ pulse$^{-1}$). The photoconductivity ($\Delta\sigma = A^{-1}\,\Delta P_r\,P_r^{-1}$ where $A$ is the sensitivity factor, $P_r$ is the reflected microwave power, and $\Delta P_r$ is the change in $P_r$ upon exposure to light) was converted into the product of the quantum yield ($\varphi$) and sum of the charge carrier mobilities $\Sigma\mu$ ($= \mu_+ + \mu_-$) using the relationship $\varphi\Sigma\mu = \Delta\sigma(eI_0F_{light})^{-1}$, where $e$ and $F_{Light}$ are the electron charge and correction (or filling) factor, respectively. The experiments were performed at room temperature in the air.

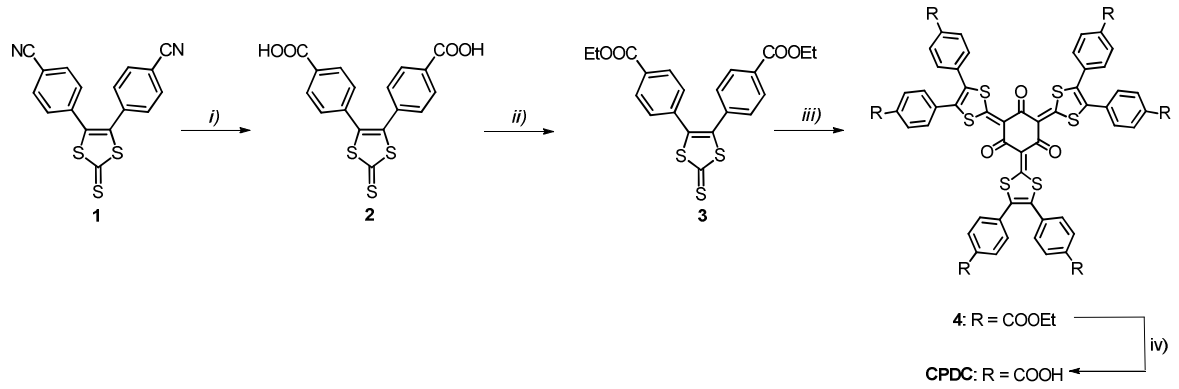
## 2. Synthetic details

**Scheme S1**. Synthesis of 4,4'-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzonitrile **1**.[a]




[a] Reagents and conditions: (i) (a) 1.0 M TMP.MgCl.LiCl, dry THF, -78 °C, 0.5 h, (b) 1.0 M $ZnCl_2$, -78 °C, 0.25 h, (c) 4-iodobenzonitrile, $Pd(PPh_3)_4$, dry NMP, 25 °C, 18 h, 85%; (ii) (a) 1.0 M TMP.MgCl.LiCl, dry THF, -78 °C, 0.5 h, (b) 1.0 M $ZnCl_2$, -78 °C, 0.25 h, 43-44%. Ref. [S4]

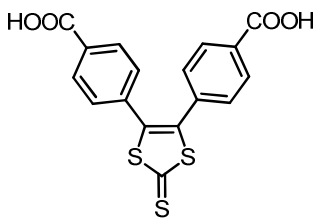
**Scheme S2**. Synthesis of **CPDC**.[a]




[a] Reagents and conditions: (i) conc. $H_2SO_4$, $H_2O$, AcOH, 100 °C, 13 h, 54%; (ii) EtOH, conc. $H_2SO_4$, reflux, 20 h, 93%; (iii) phloroglucinol, $Et_3N$, $AgNO_3$, dry MeCN, 75 °C, 12 h, 86%; (iv) 10% KOH, THF, 50 °C, 48-72 h, 99%.

Compound **1** was synthesized from 1,3-dithiole-2-thione by following the literature procedure (Scheme S1).[S4]

### 4,4'-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzoic acid (2)

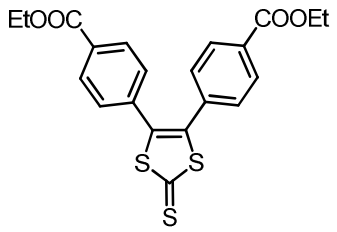



Dibenzonitrile **1** (142 mg, 422 μmol) was dissolved in hot AcOH (3 mL) and was followed by addition of $H_2O$ (1 mL) and conc. sulfuric acid (1 mL) at 0 °C. The suspension was heated to 100 °C for 13 h. Thereupon, the reaction mixture was cooled and 2M KOH (50 mL) was added to basify the solution to pH 14. EtOAc extraction (50 mL, 2x) was carried out to remove organic impurities. The aqueous layer was then acidified to pH 1 using conc. hydrochloric acid and the precipitate obtained was filtered, washed with distilled water and dried to obtain **2** (85 mg, 54%) as reddish brown solid, which was recrystallized using dichloromethane.

**2.** mp > 300 °C; $^1$H NMR (396 MHz, DMSO-$d_6$) δ 7.43 (m, 4H), 7.91 (m, 4H), 13.15 (br. s). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 129.7, 130.0, 131.7, 133.5, 139.3, 166.5, 209.4; IR (KBr) ν

2959*w*, 1685*s*, 1605*m*, 1424*s*, 1285*s*; ESI HRMS, m/z 372.96750 [(M-H)$^+$, 100, calcd 372.96684].

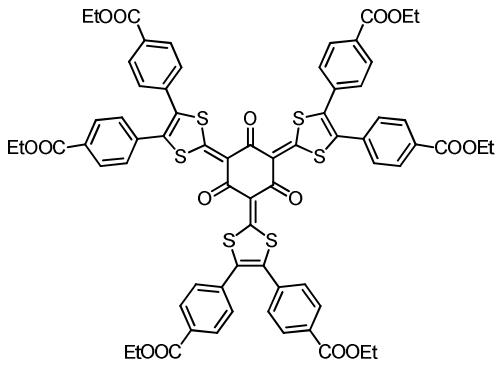
**Diethyl 4,4'-(2-thioxo-1,3-dithiole-4,5-diyl)dibenzoate (3)**




To a suspension of dibenzoic acid **2** (56 mg, 150 μmol) in EtOH (5 mL), 0.25 mL of conc. sulfuric acid was added, and the reaction mixture was refluxed for 20 h. After cooling to ambient temperature, $CHCl_3$ (25 mL) was added. The organic layer was washed with 5% $NaHCO_3$ (25 mL, 2x), brine (25 mL, 2x), and water (25 mL, 1x) before being dried ($Na_2SO_4$). The product was isolated by column chromatography ($SiO_2$; $CHCl_3$/hexane 3:7) to obtain **3** (60 mg, 93%) as yellow solid.

**3.** mp 141-143 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.1 Hz, 6H), 4.36 (q, *J* = 7.2 Hz, 4H), 7.27 (d, *J* = 8.5 Hz, 4H), 7.96 (d, *J* = 8.5 Hz, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.4, 61.5, 129.3, 130.4, 131.5, 134.4, 139.3, 165.7, 209.8; IR (KBr) ν 2980*w*, 1720*s*, 1605*m*, 1406*s*, 1277*s*, 1177*m*; ESI HRMS, m/z 453.02615 [(M+Na)$^+$, 100, calcd 453.02594].

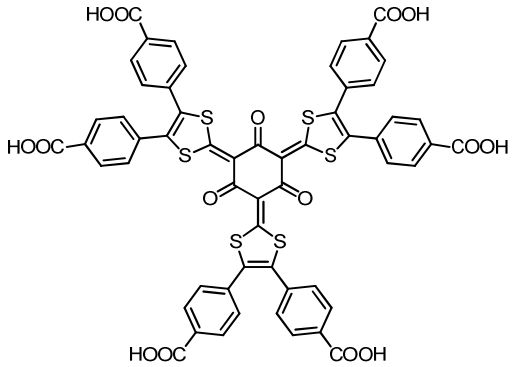
**Hexaethyl 4,4',4'',4''',4'''',4'''''-(2,2',2''-(2,4,6-trioxocyclohexane-1,3,5-triylidene)tris(1,3-dithiole-4,5-diyl-2-ylidene)) hexabenzoate (4)**




To the stirred solution of phloroglucinol (22 mg, 173 μmol) and **3** (224 mg, 520 μmol) in anhydrous acetonitrile (5 mL), triethylamine (290 μL, 2.081 mmol) was added dropwise followed by silver nitrate (177 mg, 1.04 mmol). The reaction mixture was heated to 75 °C for 12 h. After being cooled to room temperature, the solvent was stripped off in vacuo. The product was isolated by performing column chromatography ($SiO_2$; 100% $CHCl_3$) to afford dark yellow solid **4** (195 mg, 86%).

**4.** mp > 300 °C; $^1$H NMR (396 MHz, $CDCl_3$) δ 1.4 (t, *J* = 7.1 Hz, 18H) 4.4 (q, *J* =7.2 Hz, 12H) 7.4 (d, *J* = 8.2 Hz, 12H) 7.8 (d, *J* = 8.5 Hz, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.4, 61.3, 114.9, 129.7, 130.0, 130.9, 135.5, 137.2, 165.8, 171.6, 175.9; IR (KBr) ν 2980*w*, 1720*s*, 1606*m*, 1537*s*, 1421*s*, 1107*s* cm$^{-1}$ ; ESI HRMS, m/z 1337.16524 [(M+Na)$^+$, 100, calcd 1337.16846].

**4,4',4'',4''',4'''',4'''''-(2,2',2''-(2,4,6-trioxocyclohexane-1,3,5-triylidene)tris(1,3-dithiole-4,5-diyl-2-ylidene))hexabenzoic acid (CPDC)**




To a suspension of ethyl ester of hexabenzoic acid **4** (110 mg, 84 μmol) in THF (14 mL), 10% aq. KOH (5 mL) was added. The reaction mixture was heated to 50 °C and stirred at this temperature until the solution became clear (2-3 days). Subsequently, THF was evaporated in vacuo and the aqueous layer was acidified to pH 1 using conc. HCl and filtered. The precipitate was dried under vacuum to obtain **CPDC** (95 mg, 99%) as yellow colored solid.

**CPDC.** mp >300 °C; $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 7.29 (d, $J$ = 7.6 Hz, 12H), 7.73 (d, $J$ = 7.6 Hz, 12H), 12.98 (br. s); $^{13}$C NMR spectrum could not be obtained due to poor solubility; IR (KBr) ν 2966*w*, 1694*s*, 1607*m*, 1534*s*, 1410*s*, 1102*m*, 644*m* cm$^{-1}$; ESI HRMS, m/z 1144.98273 [(M-H)$^{-}$, 100, calcd 1144.98307].

## 3. NMR spectra

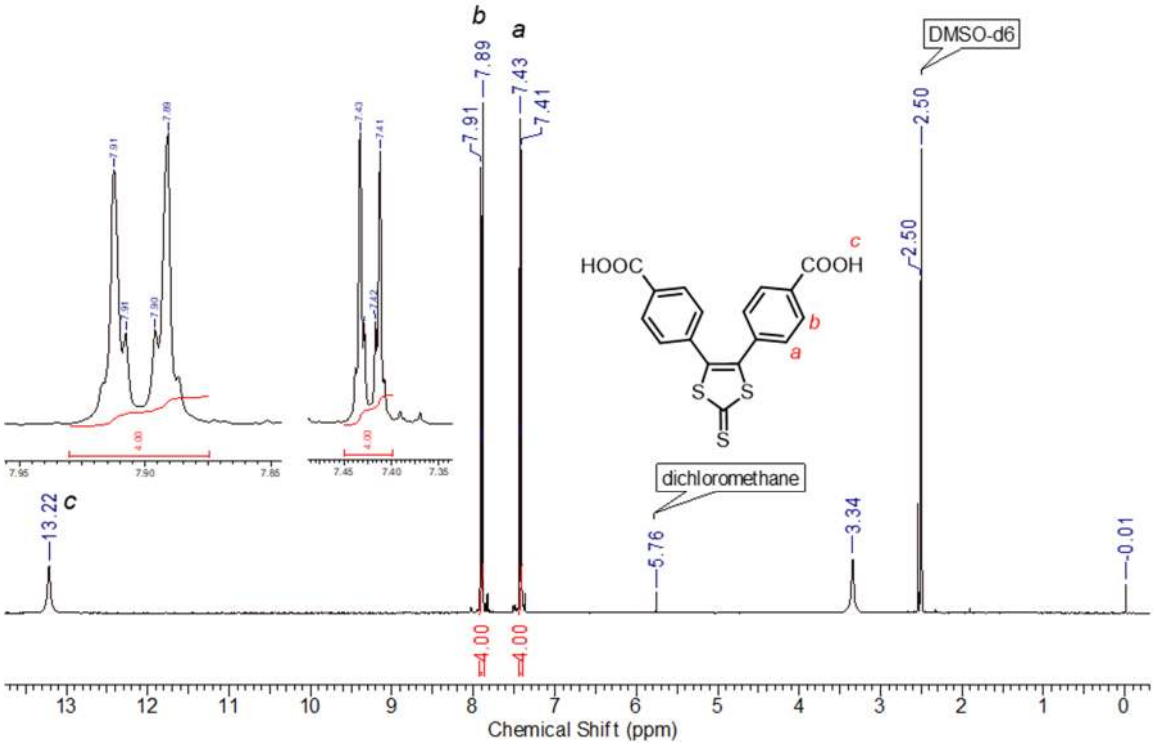



**Fig. S1** $^{1}$H NMR (400 MHz, DMSO-$d_6$) spectrum of **2**.

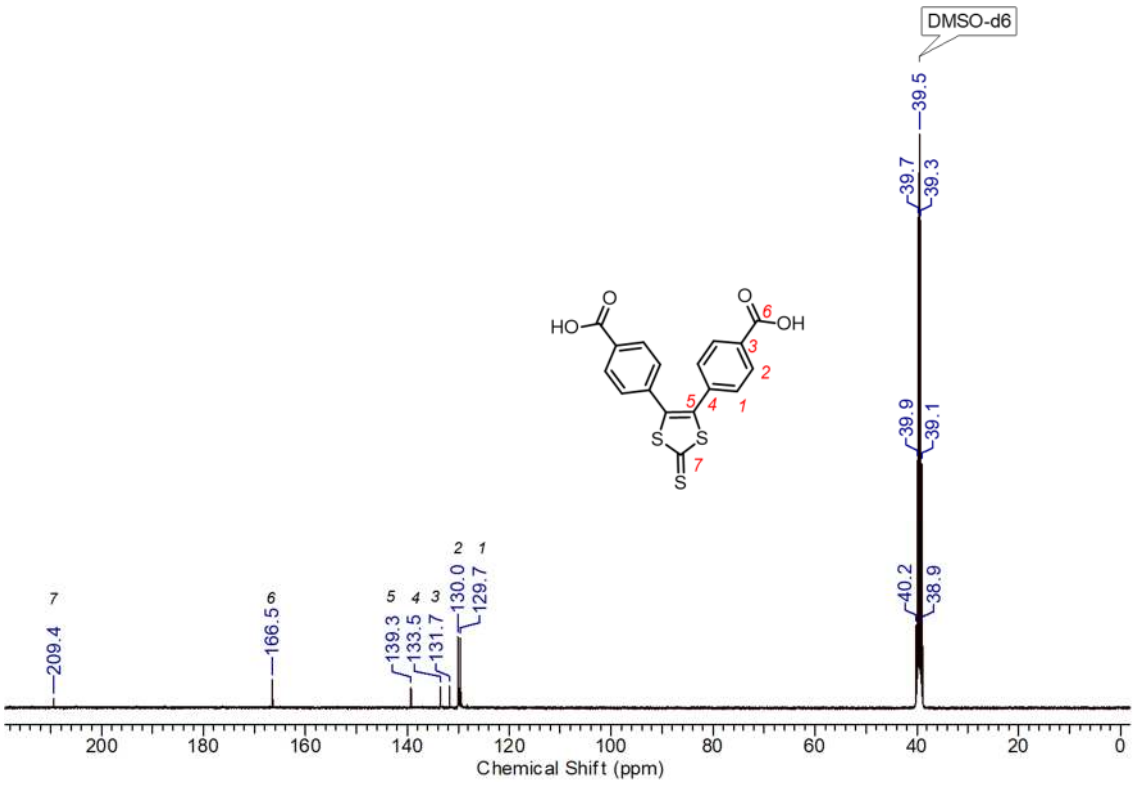



**Fig. S2** $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of **2**.

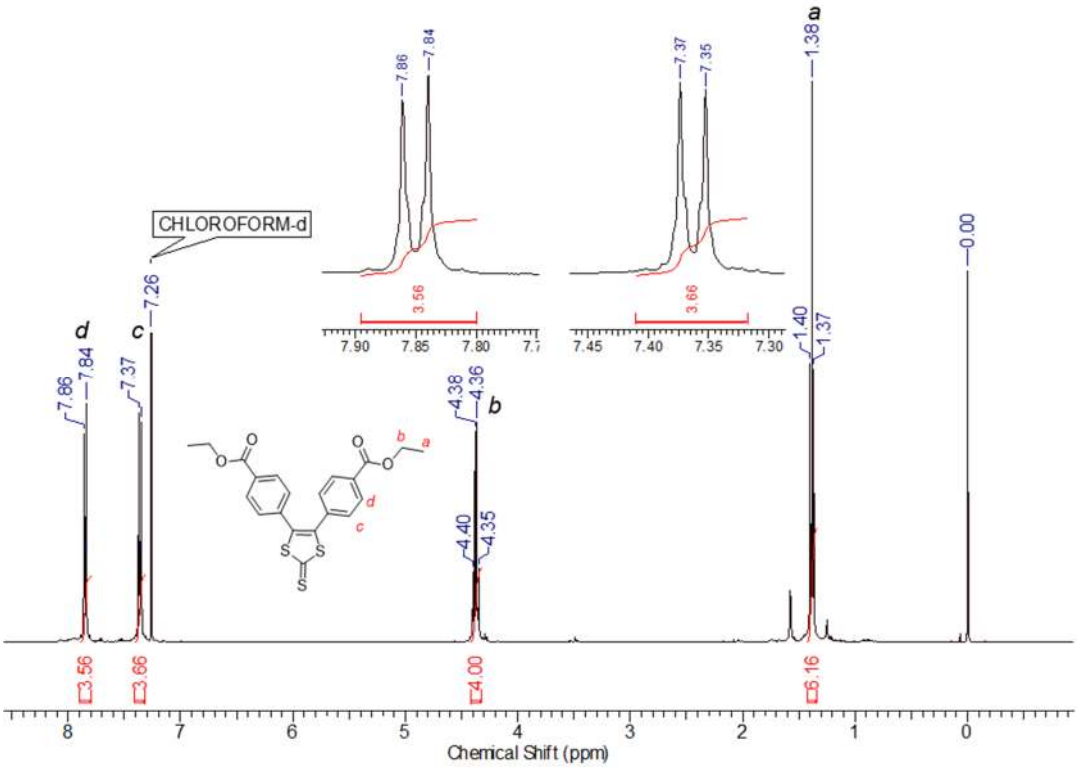



**Fig. S3** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **3**.

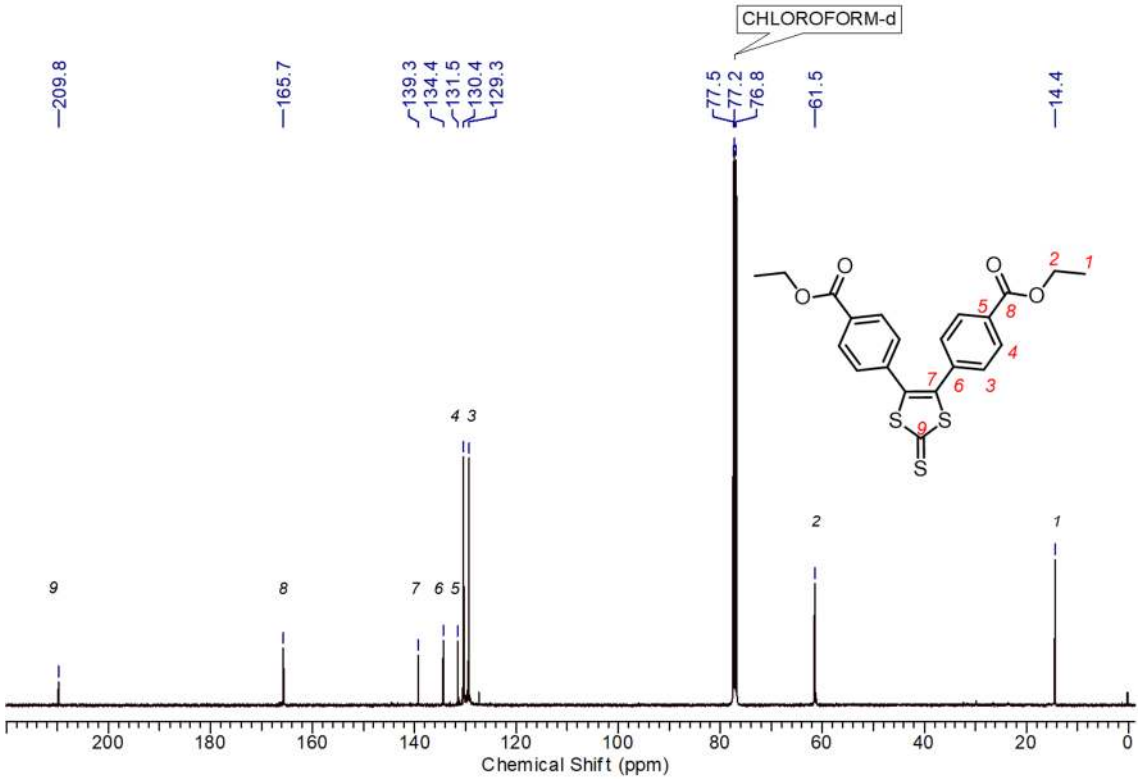



**Fig. S4** $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of **3**.

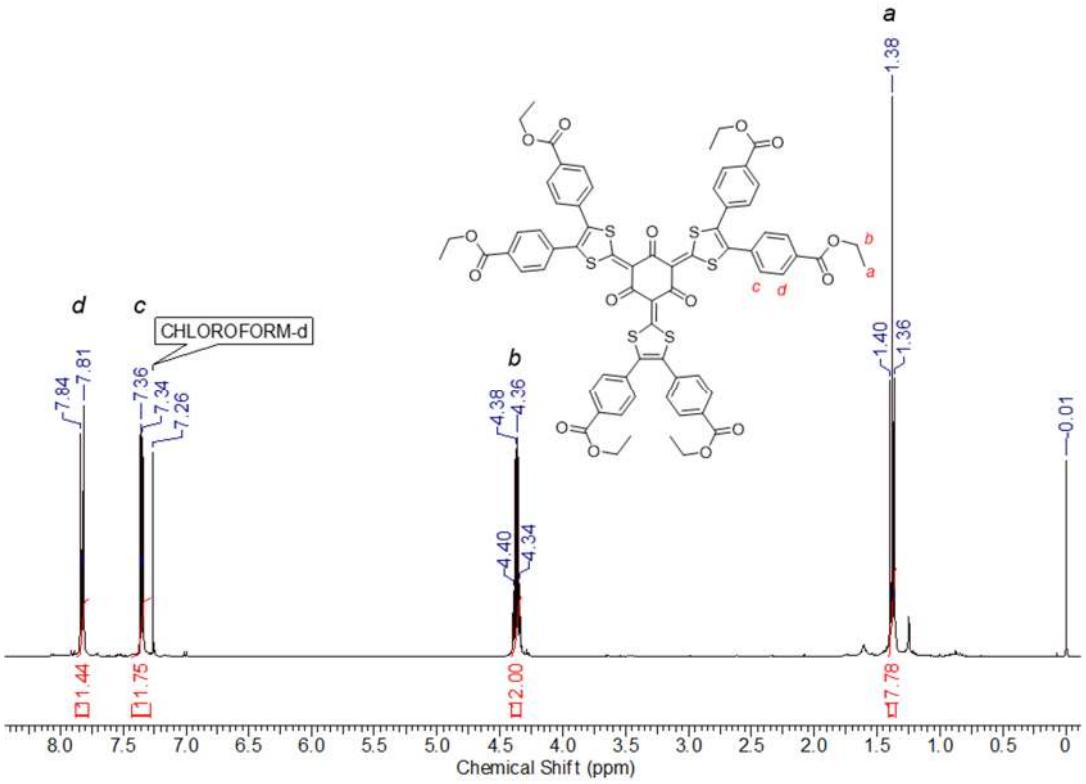



**Fig. S5** $^{1}$H NMR (400 MHz, $CDCl_3$) spectrum of **4**.

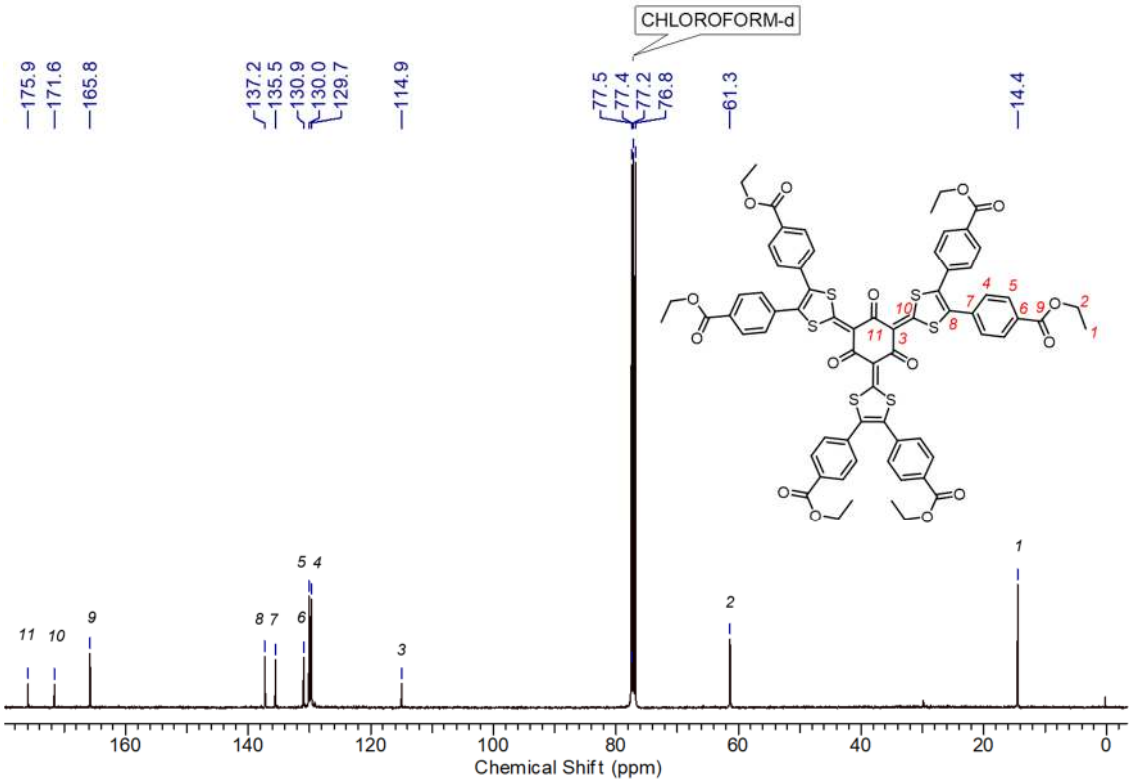



**Fig. S6** $^{13}$C NMR (100 MHz, $CDCl_3$) spectrum of **4**.

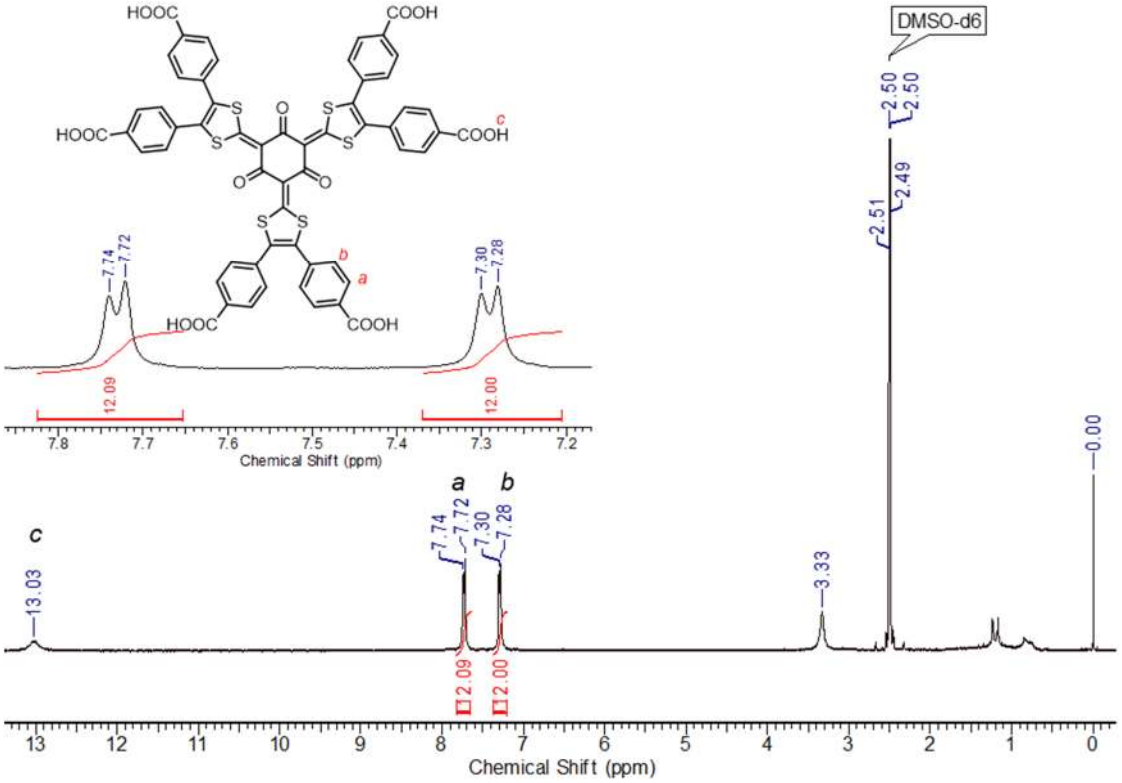



**Fig. S7** $^{1}$H NMR (400 MHz, DMSO-$d_6$) spectrum of **CPDC**.

## 4. Absorption and Emission Spectra

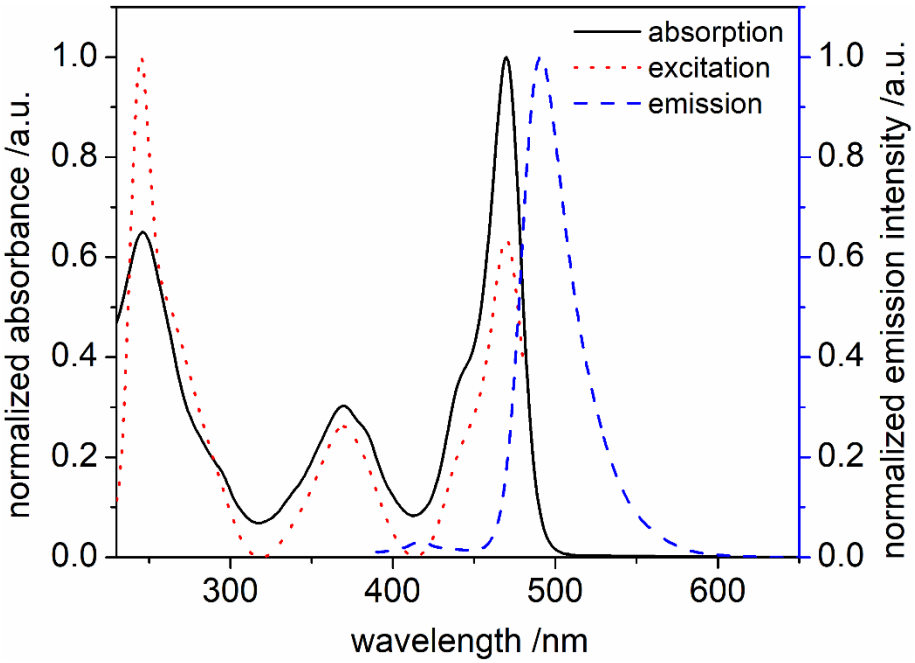



**Fig. S8** UV-vis, excitation and emission spectra of **4** obtained from its solution in dichloromethane. The excitation wavelength used is 370 nm. Optical band gap ($E_g$) was determined from the absorption edge: $E_g = 1240/\lambda_{onset}$, apparent absorption edge ($\lambda_{onset}$) at 488 nm.

## 5. Electrochemical studies

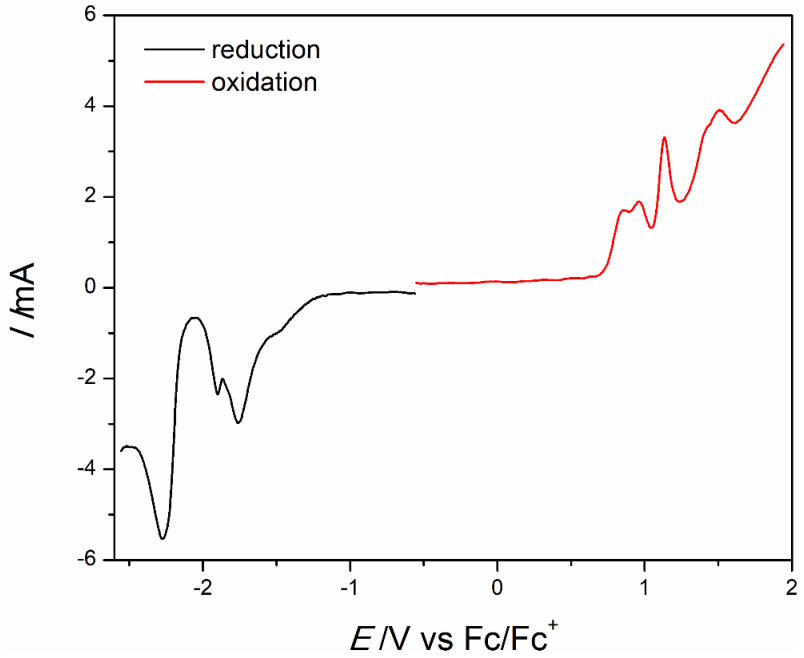



**Fig. S9** Differential pulse voltammogram of **4** obtained from its 0.49 mM solution in dichloromethane using $TBABF_4$ as supporting electrolyte, and platinum electrodes as working and counter electrodes.

**Table S1**. Electrochemical data of **4** versus $Fc/Fc^+$.

| Compound | $E_{ox}$ (V) | $E_{red}$ (V) | $E_{HOMO}$ [a] (eV) | $E_{LUMO}$ [b] (eV) | Electrochemical band gap ($E_g$) (eV) |
|---|---|---|---|---|---|
| **4** | 0.85, 0.96<br>1.13<br>1.41, 1.50 | -1.75<br>-1.90<br>-2.28 | -5.82 | -3.57 | 2.25 |

[a]Estimated from the onset of oxidation (0.72 V): $E_{HOMO} = -[E_{(onset\ ox\ vs\ Fc/Fc+)} + 5.1]$ /eV. [b]Estimated from the onset of reduction (-1.53 V) $E_{LUMO} = -[E_{(onset\ ox\ vs\ Fc/Fc+)} + 5.1]$ /eV. Electrochemical band gap was calculated using the formula $E_g = E_{HOMO}-E_{LUMO}$.[S5]

## 6. Theoretical calculation

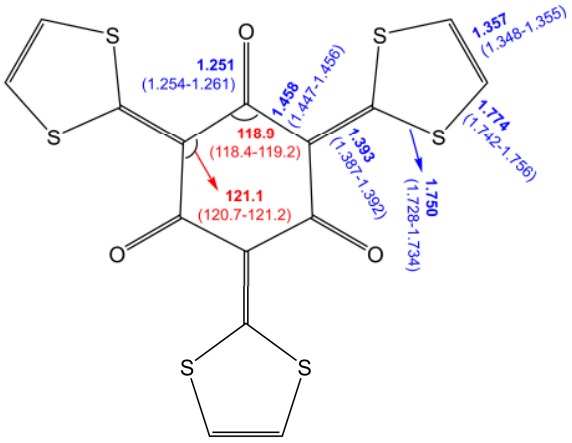



**Fig. S10** Selected bond lengths (blue) and angles (red) of the DC core. Theoretical values calculated at the B3LYP/6-31G** level are shown in bold font and observed values in the crystal structure are shown in parentheses.

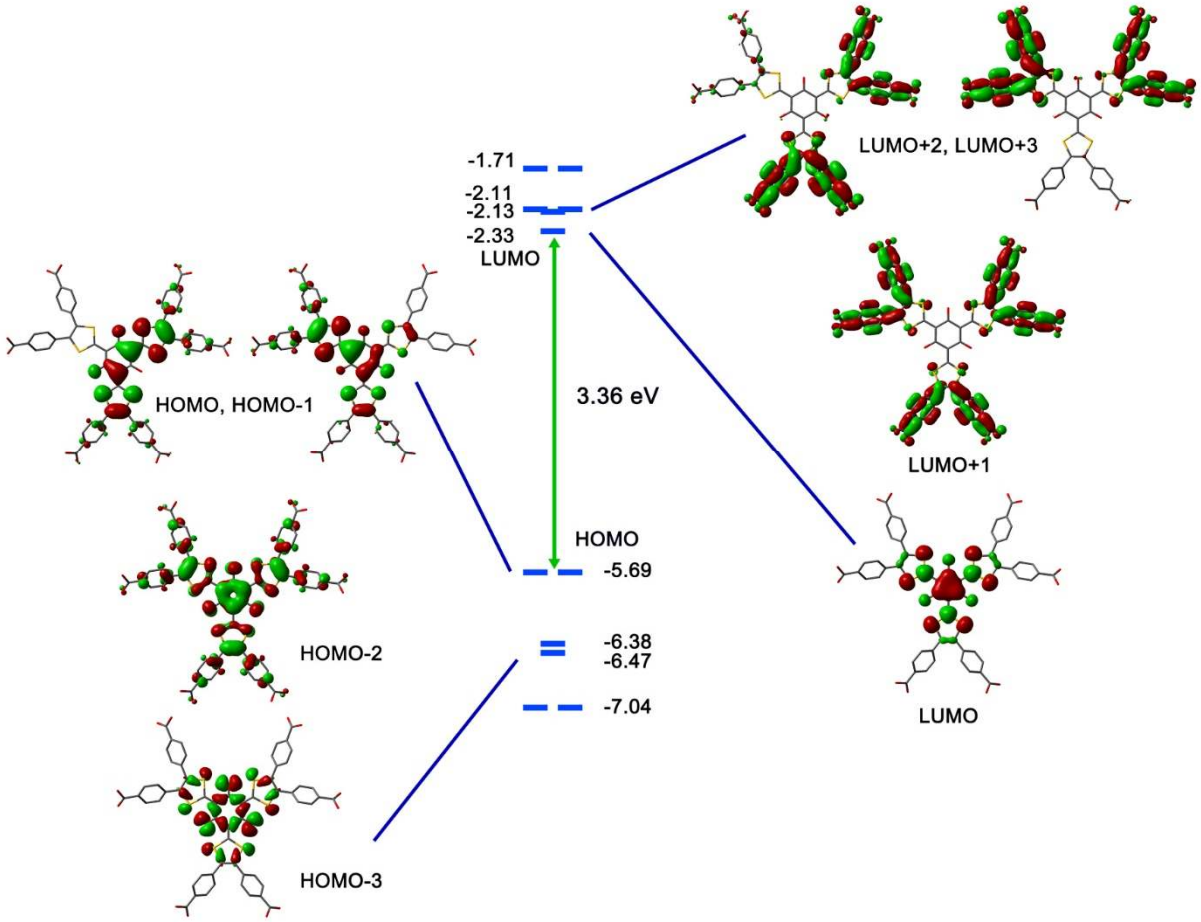



**Fig. S11**. Selected molecular orbitals and energy levels of **CPDC** calculated at the B3LYP/6-31G** level of theory.

**Table S2.** Atomic coordinates of **CPDC** molecule.

| Coordinates (Angstroms) | | | | Coordinates (Angstroms) | | | | Coordinates (Angstroms) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | X | Y | Z | | X | Y | Z | | X | Y | Z |
| C | 1.351092 | -0.568262 | -0.018407 | C | -7.164758 | 0.074873 | -0.759059 | H | -0.846413 | -9.644072 | -1.777982 |
| C | -1.336422 | 0.562104 | -0.017366 | C | -7.503992 | 1.673199 | 1.027556 | H | -3.443402 | -8.264946 | 1.342372 |
| C | 0.181415 | -1.438427 | -0.017366 | C | -8.836393 | 1.292461 | 1.112433 | C | 2.393014 | -6.296061 | 0.083326 |
| C | 1.155007 | 0.876323 | -0.017366 | C | -8.499806 | -0.308514 | -0.672722 | C | 4.412483 | -8.243155 | 0.263104 |
| C | -0.183417 | 1.454211 | -0.018407 | H | -6.518359 | -0.394408 | -1.494053 | C | 2.302963 | -7.335247 | 1.027556 |
| C | -1.167676 | -0.885949 | -0.018407 | H | -7.112506 | 2.429106 | 1.699163 | C | 3.517537 | -6.242299 | -0.759059 |
| O | 2.504753 | -1.053512 | -0.019322 | H | -9.501721 | 1.745884 | 1.838989 | C | 4.517084 | -7.206790 | -0.672722 |
| O | -2.164745 | -1.642424 | -0.019322 | H | -8.890134 | -1.076426 | -1.330268 | C | 3.298892 | -8.298771 | 1.112433 |
| O | -0.340009 | 2.695936 | -0.019322 | C | 4.256042 | 5.220441 | 0.083326 | H | 1.452586 | -7.374164 | 1.699163 |
| C | 0.355803 | -2.820152 | -0.012840 | C | 4.932540 | 7.942899 | 0.263104 | H | 3.600746 | -5.447861 | -1.494053 |
| C | 2.264422 | 1.718211 | -0.012840 | C | 5.201029 | 5.662048 | 1.027556 | H | 5.377279 | -7.160869 | -1.330268 |
| C | -2.620225 | 1.101941 | -0.012840 | C | 3.647221 | 6.167426 | -0.759059 | H | 3.238881 | -9.101674 | 1.838989 |
| S | 1.933261 | -3.577147 | 0.005502 | C | 3.982721 | 7.515305 | -0.672722 | C | 5.449565 | -9.300034 | 0.400034 |
| S | -0.984235 | -3.945237 | -0.022846 | C | 5.537501 | 7.006310 | 1.112433 | O | 5.403733 | -10.216897 | 1.195572 |
| S | -2.924558 | 2.824991 | -0.022846 | H | 5.659920 | 4.945059 | 1.699163 | O | 6.481066 | -9.146568 | -0.467604 |
| S | -4.064531 | 0.114320 | 0.005502 | H | 2.917612 | 5.842268 | -1.494053 | H | 7.089726 | -9.882090 | -0.287864 |
| S | 2.131270 | 3.462827 | 0.005502 | H | 3.512854 | 8.237295 | -1.330268 | C | -3.034804 | -10.331968 | -0.255731 |
| S | 3.908793 | 1.120247 | -0.022846 | H | 6.262840 | 7.355790 | 1.838989 | O | -3.994624 | -10.556123 | 0.454315 |
| C | 1.346213 | -5.251631 | 0.006729 | C | 6.174575 | 2.693607 | -0.066322 | O | -2.594625 | -11.223168 | -1.178865 |
| C | 0.000000 | -5.421749 | -0.005035 | C | 8.980629 | 2.616048 | -0.218475 | H | -3.190166 | -11.987895 | -1.113310 |
| C | -4.695372 | 2.710874 | -0.005035 | C | 6.914167 | 1.838050 | 0.770572 | C | -10.778848 | -0.069444 | 0.400034 |
| C | -5.221153 | 1.459961 | 0.006729 | C | 6.864259 | 3.499706 | -0.989355 | O | -11.549959 | 0.428678 | 1.195572 |
| C | 3.874939 | 3.791670 | 0.006729 | C | 8.251888 | 3.465683 | -1.062386 | O | -11.161694 | -1.039484 | -0.467604 |
| C | 4.695372 | 2.710874 | -0.005035 | C | 8.301666 | 1.801997 | 0.696058 | H | -12.103005 | -1.198838 | -0.287864 |
| C | -5.420019 | 4.000535 | -0.066322 | H | 6.397744 | 1.211227 | 1.490716 | C | -7.430345 | 7.794201 | -0.255731 |
| C | -6.755878 | 6.469429 | -0.218475 | H | 6.304157 | 4.146124 | -1.655722 | O | -7.144558 | 8.737507 | 0.454315 |
| C | -6.462964 | 4.194769 | -0.989355 | H | 8.775218 | 4.089021 | -1.777982 | O | -8.422236 | 7.858595 | -1.178865 |
| C | -5.048881 | 5.068819 | 0.770572 | H | 8.879354 | 1.150399 | 1.342372 | H | -8.786739 | 8.756712 | -1.113310 |
| C | -5.711409 | 6.288455 | 0.696058 | C | -0.754555 | -6.694142 | -0.066322 | C | 5.329284 | 9.369478 | 0.400034 |
| C | -7.127314 | 5.413503 | -1.062386 | C | -2.224751 | -9.085477 | -0.218475 | O | 6.146226 | 9.788219 | 1.195572 |
| H | -6.742727 | 3.386499 | -1.655722 | C | -1.865285 | -6.906869 | 0.770572 | O | 4.680628 | 10.186052 | -0.467604 |
| H | -4.247825 | 4.934995 | 1.490716 | C | -0.401295 | -7.694475 | -0.989355 | H | 5.013278 | 11.080928 | -0.287864 |
| H | -5.435952 | 7.114546 | 1.342372 | C | -1.124574 | -8.879186 | -1.062386 | C | 10.465148 | 2.537767 | -0.255731 |
| H | -7.928805 | 5.555051 | -1.777982 | C | -2.590258 | -8.090453 | 0.696058 | O | 11.139182 | 1.818615 | 0.454315 |
| C | -6.649056 | 1.075620 | 0.083326 | H | -2.149919 | -6.146222 | 1.490716 | O | 11.016861 | 3.364573 | -1.178865 |
| C | -9.345023 | 0.300256 | 0.263104 | H | 0.438570 | -7.532622 | -1.655722 | H | 11.976905 | 3.231183 | -1.113310 |

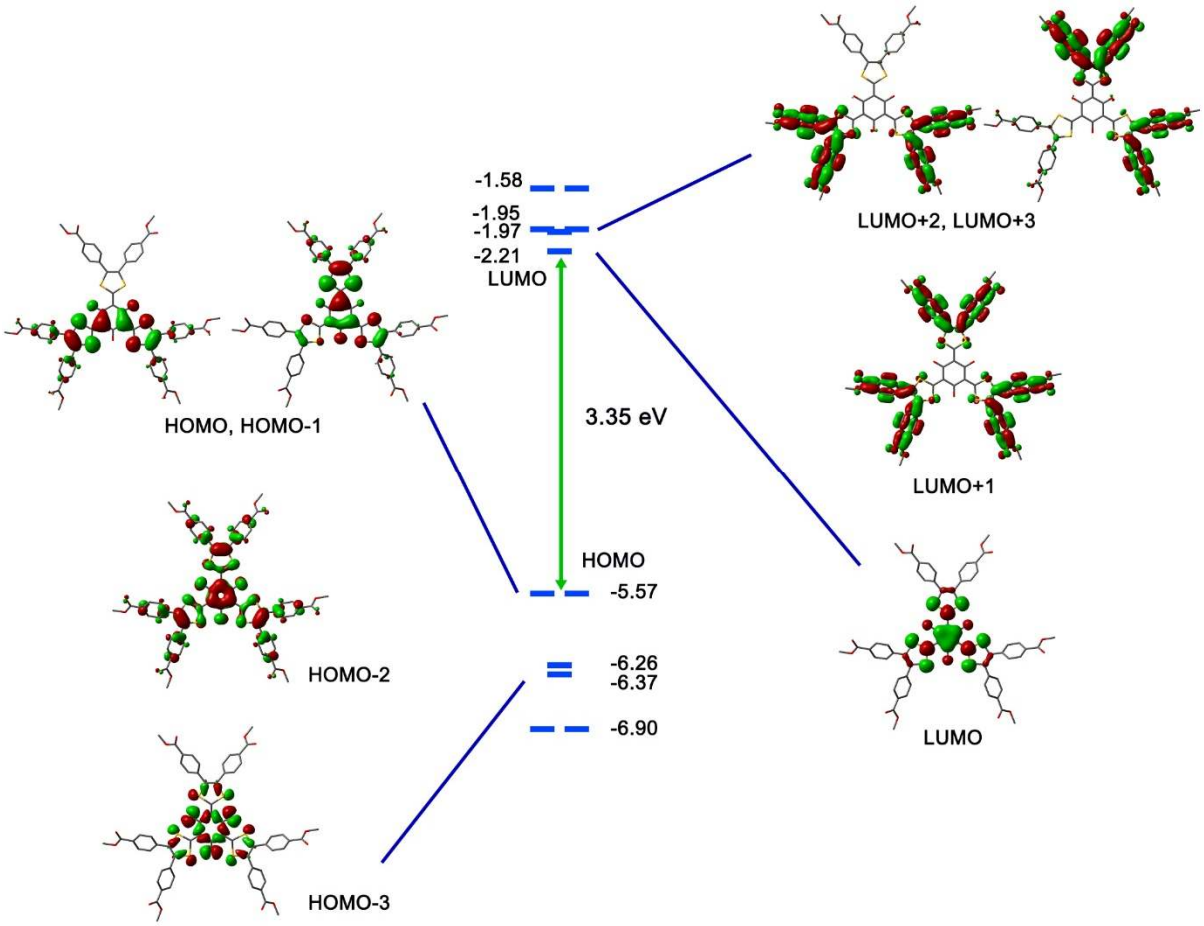



**Fig. S12**. Selected molecular orbitals and energy levels of methyl ester derivative of **CPDC** calculated at the B3LYP/6-31G** level of theory.

**Table S3.** Atomic coordinates of the methyl ester derivative of **CPDC**.

| Coordinates (Angstroms) | | | | Coordinates (Angstroms) | | | | Coordinates (Angstroms) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | X | Y | Z | | X | Y | Z | | X | Y | Z |
| 6C | -0.345258 | 1.424477 | 0.012853 | 1H | 4.239555 | -8.676016 | 1.894950 | 6C | 4.246443 | 9.912038 | 0.462367 |
| 6C | 0.341519 | -1.409046 | 0.014519 | 1H | 6.148225 | -6.517026 | -1.277604 | 8O | 5.017102 | 10.407247 | 1.261249 |
| 6C | 1.049510 | 1.000287 | 0.014519 | 6C | -6.728120 | 0.323425 | 0.131194 | 8O | 3.504296 | 10.642635 | -0.400657 |
| 6C | -1.391029 | 0.408758 | 0.014519 | 6C | -9.320711 | -0.751233 | 0.317765 | 6C | 10.122072 | 3.697544 | -0.147328 |
| 6C | -1.061004 | -1.011241 | 0.012853 | 6C | -7.642293 | 0.819721 | 1.078286 | 8O | 10.856300 | 3.058128 | 0.580300 |
| 6C | 1.406262 | -0.413236 | 0.012853 | 6C | -7.131287 | -0.727944 | -0.710907 | 8O | 10.576243 | 4.576569 | -1.069385 |
| 8O | -0.640079 | 2.640873 | 0.011865 | 6C | -8.414334 | -1.259457 | -0.620846 | 6C | 6.460855 | -8.633546 | 0.462367 |
| 8O | 2.607103 | -0.766112 | 0.011865 | 6C | -8.923407 | 0.291315 | 1.166078 | 8O | 6.504390 | -9.548561 | 1.261249 |
| 8O | -1.967024 | -1.874761 | 0.011865 | 1H | -7.336434 | 1.614334 | 1.749663 | 8O | 7.464644 | -8.356127 | -0.400657 |
| 6C | 2.057727 | 1.961233 | 0.022660 | 1H | -6.438629 | -1.120899 | -1.448620 | 6C | -1.858869 | -10.614744 | -0.147328 |
| 6C | -2.727341 | 0.801427 | 0.022660 | 1H | -8.718022 | -2.066006 | -1.277604 | 8O | -2.779733 | -10.930896 | 0.580300 |
| 6C | 0.669615 | -2.762660 | 0.022660 | 1H | -9.633428 | 0.666445 | 1.894950 | 8O | -1.324697 | -11.447580 | -1.069385 |
| 6S | 1.730239 | 3.680005 | 0.041206 | 6C | -5.834718 | 3.368676 | -0.005970 | 6C | -10.707298 | -1.278492 | 0.462367 |
| 6S | 3.758974 | 1.551785 | 0.019154 | 6C | -7.442423 | 5.673114 | -0.130131 | 8O | -11.521492 | -0.858686 | 1.261249 |
| 6S | -0.535602 | -4.031260 | 0.019154 | 6C | -5.587402 | 4.461681 | 0.844222 | 8O | -10.968940 | -2.286508 | -0.400657 |
| 6S | 2.321858 | -3.338433 | 0.041206 | 6C | -6.892104 | 3.455761 | -0.928744 | 6C | -8.263203 | 6.917199 | -0.147328 |
| 6S | -4.052097 | -0.341572 | 0.041206 | 6C | -7.690271 | 4.592265 | -0.987812 | 8O | -8.076567 | 7.872768 | 0.580300 |
| 6S | -3.223373 | 2.479474 | 0.019154 | 6C | -6.384264 | 5.599240 | 0.783479 | 8O | -9.251547 | 6.871011 | -1.069385 |
| 6C | 3.426145 | 4.202650 | 0.050985 | 1H | -4.776502 | 4.410259 | 1.564032 | 6C | 8.606196 | -9.223439 | -0.309499 |
| 6C | 4.362286 | 3.220472 | 0.043139 | 1H | -7.078136 | 2.629179 | -1.605482 | 1H | 9.047222 | -9.174274 | 0.688912 |
| 6C | 0.607868 | -5.388086 | 0.043139 | 1H | -8.502437 | 4.651426 | -1.702701 | 1H | 9.310331 | -8.861638 | -1.058260 |
| 6C | 1.926529 | -5.068453 | 0.050985 | 1H | -6.204900 | 6.443038 | 1.440616 | 1H | 8.320902 | -10.257508 | -0.517582 |
| 6C | -5.352674 | 0.865803 | 0.050985 | 6C | 5.834718 | 3.368676 | -0.005970 | 6C | 12.005073 | 4.710565 | -1.133903 |
| 6C | -4.970153 | 2.167614 | 0.043139 | 6C | 8.634272 | 3.608770 | -0.130131 | 1H | 12.402368 | 5.053328 | -0.175520 |
| 6C | 0.000000 | -6.737352 | -0.005970 | 6C | 6.657630 | 2.607991 | 0.844222 | 1H | 12.195955 | 5.447139 | -1.913890 |
| 6C | -1.191850 | -9.281884 | -0.130131 | 6C | 6.438828 | 4.240857 | -0.928744 | 1H | 12.469863 | 3.754274 | -1.385681 |
| 6C | 0.453276 | -7.696617 | -0.928744 | 6C | 7.822154 | 4.363838 | -0.987812 | 6C | 3.684635 | 12.064904 | -0.309499 |
| 6C | -1.070229 | -7.069672 | 0.844222 | 6C | 8.041215 | 2.729315 | 0.783479 | 1H | 3.019238 | 12.493802 | -1.058260 |
| 6C | -1.656952 | -8.328554 | 0.783479 | 1H | 6.207647 | 1.931442 | 1.564032 | 1H | 4.722811 | 12.334867 | -0.517582 |
| 6C | -0.131882 | -8.956103 | -0.987812 | 1H | 5.816004 | 4.815256 | -1.605482 | 1H | 3.421543 | 12.422261 | 0.688912 |
| 1H | 1.262132 | -7.444436 | -1.605482 | 1H | 8.279472 | 5.037613 | -1.702701 | 6C | -10.082005 | 8.041415 | -1.133903 |
| 1H | -1.431145 | -6.341701 | 1.564032 | 1H | 8.682285 | 2.152082 | 1.440616 | 1H | -9.486229 | 8.922081 | -1.385681 |
| 1H | -2.477384 | -8.595121 | 1.440616 | 6C | 3.644154 | 5.665010 | 0.131194 | 1H | -10.577494 | 8.214102 | -0.175520 |
| 1H | 0.222965 | -9.689039 | -1.702701 | 6C | 4.009769 | 8.447590 | 0.317765 | 1H | -10.815338 | 7.838437 | -1.913890 |
| 6C | 3.083965 | -5.988435 | 0.131194 | 6C | 4.531045 | 6.208559 | 1.078286 | 6C | -12.290831 | -2.841465 | -0.309499 |
| 6C | 5.310943 | -7.696356 | 0.317765 | 6C | 2.935225 | 6.539847 | -0.710907 | 1H | -13.043714 | -2.077359 | -0.517582 |
| 6C | 4.196061 | -5.811903 | -0.710907 | 6C | 3.116446 | 7.916756 | -0.620846 | 1H | -12.468765 | -3.247987 | 0.688912 |
| 6C | 3.111247 | -7.028280 | 1.078286 | 6C | 4.713989 | 7.582240 | 1.166078 | 1H | -12.329569 | -3.632164 | -1.058260 |
| 6C | 4.209417 | -7.873554 | 1.166078 | 1H | 5.066271 | 5.546371 | 1.749663 | 6C | -1.923067 | -12.751980 | -1.133903 |
| 6C | 5.297889 | -6.657299 | -0.620846 | 1H | 2.248587 | 6.136465 | -1.448620 | 1H | -2.983635 | -12.676355 | -1.385681 |
| 1H | 4.190041 | -5.015566 | -1.448620 | 1H | 2.569797 | 8.583032 | -1.277604 | 1H | -1.824874 | -13.267430 | -0.175520 |
| 1H | 2.270163 | -7.160705 | 1.749663 | 1H | 5.393873 | 8.009571 | 1.894950 | 1H | -1.380617 | -13.285576 | -1.913890 |

## 7. Crystallography

**Table S4.** Crystallographic parameters of **CPDC-1**.

| Identification code | **CPDC-1** |
|---|---|
| Crystal color and shape | orange, needle |
| Empirical formula | $C_{57}H_{30}O_{15}S_6$. $2(C_8H_8O_2)$ |
| Formula weight | 1419.51 |
| Temperature/K | 100 |
| Crystal system | monoclinic |
| space group | *C*2/*c* |
| *a* / Å | 20.5397(8) |
| *b* / Å | 42.5569(12) |
| *c* / Å | 8.5642(4) |
| $\alpha$ /° | 90 |
| $\beta$ /° | 90.348(4) |
| $\gamma$ /° | 90 |
| *V* / Å$^3$ | 7485.9(5) |
| *Z* | 4 |
| $\rho_{calc}$ / g cm$^{-3}$ | 1.259 |
| $\mu$ / mm$^{-1}$ | 2.255 |
| F(000) | 2928.0 |
| Crystal size/mm$^3$ | 0.091 × 0.019 × 0.019 |
| Radiation | 1.54184 |
| 2$\theta$ max /° | 134.138 |
| Index ranges | -24 ≤ h ≤ 24, -50 ≤ k ≤ 50, -10 ≤ l ≤ 10 |
| Independent reflections | 4338 |
| Completeness to theta = 67.069 | 97.6% |
| Goodness-of-fit on $F^2$ | 1.006 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0671, $wR_2$ = 0.2048 |
| CCDC | 2038905 |

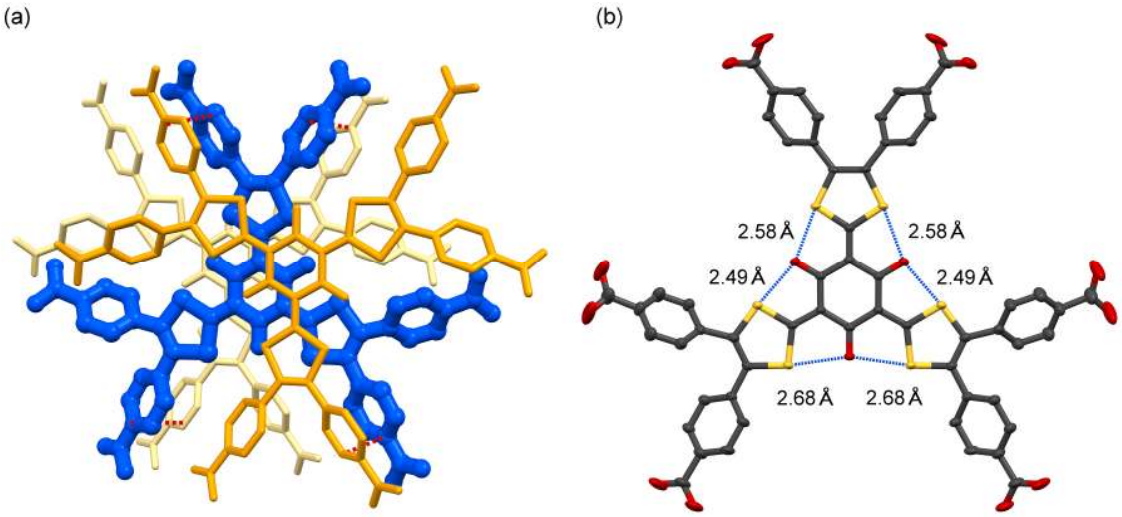



**Fig. S13** Intermolecular and intramolecular interactions in **CPDC-1**. (a) Four phenylene rings of **CPDC** involved in parallel-displaced π-stacking with a shortest distance, shown as red dashed lines, of 3.29 Å. (b) Intramolecular S···O short contacts in the range of 2.49–2.68 Å.

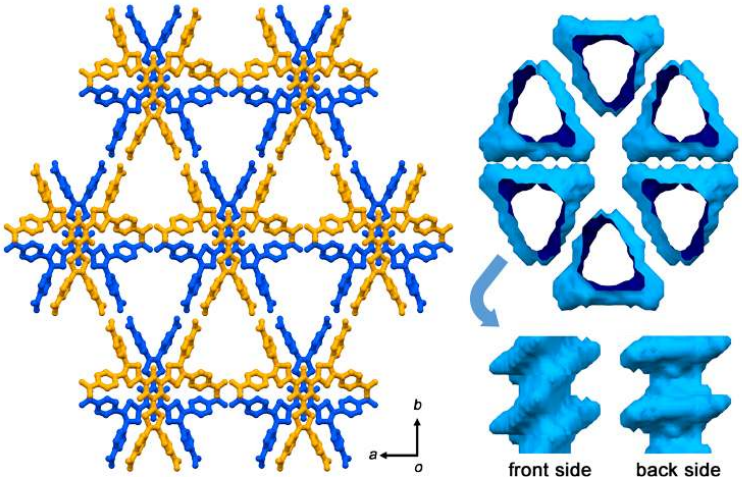



**Fig. S14** Visualized contact surface of void channels of **CPCD-1**, like a shish-kebab structure, running along the *c* axis.

## 8. TG/DTA studies

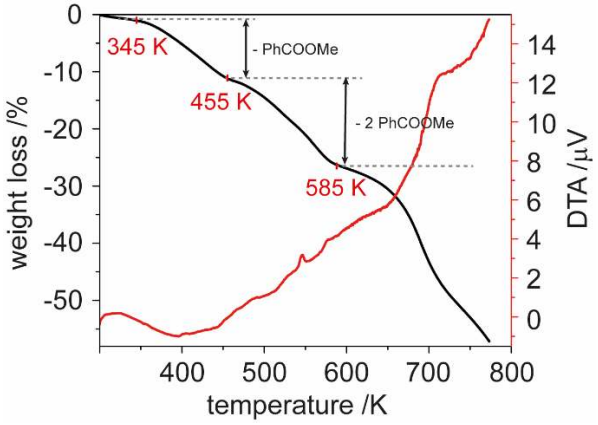



**Fig. S15** TG/DTA profile showing step-wise loss of the solvent, methyl benzoate in the as-formed crystals of **CPDC-1** obtained immediately after filtration from the mother liquor, which was followed by washing with hexane to remove the solvent molecules on the crystal surface, and drying under suction for 10 minutes.

## 9.Variable temperature - powder XRD studies

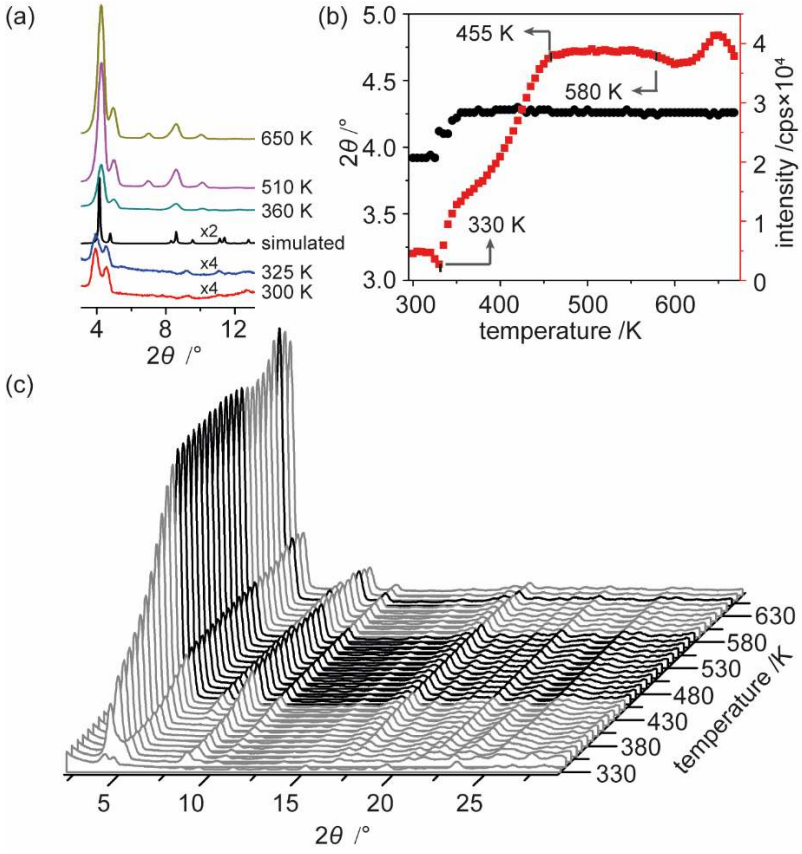



**Fig. S16** Variable temperature-PXRD measurements of as-formed crystals of **CPDC-1**. (a) Comparison of low angle peaks of simulated PXRD pattern obtained at 100 K with the PXRD patterns obtained at various higher temperatures; (b) Change in intensity and position of the 020 peak with temperature; (c) Typical PXRD patterns obtained upon heating from room temperature to 668 K. *Note*: The temperature was raised, with 5 K interval, at a rate of 2 K/min and held at desired temperature till the completion of $2\theta$ scan from 2° to 29°.

## 10. Activation of CPDC-1

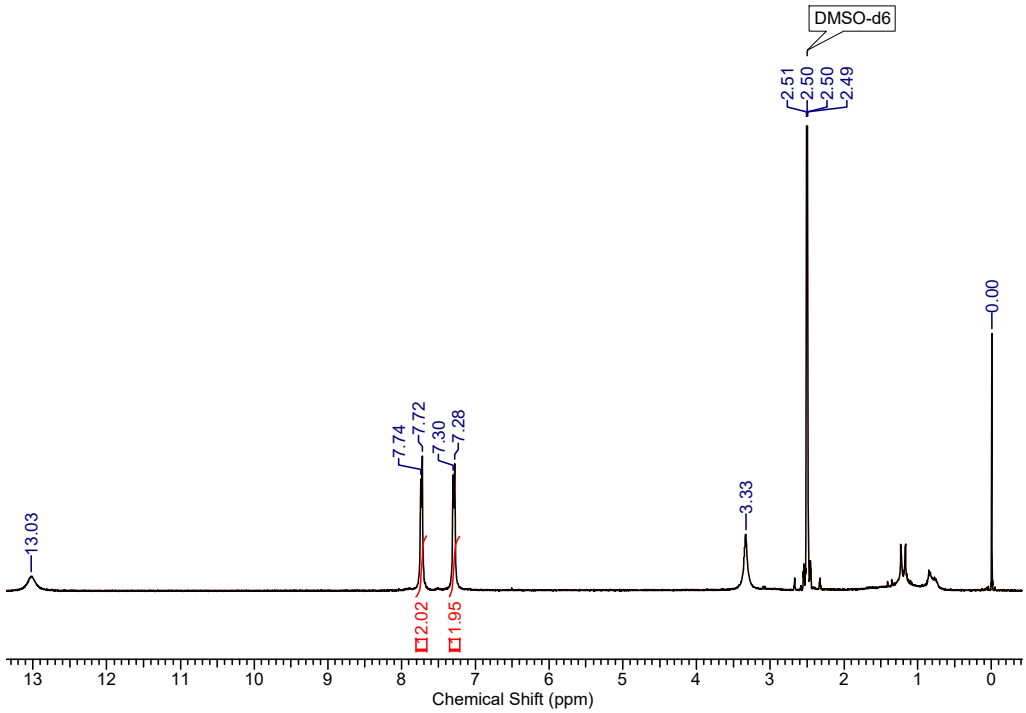



**Fig. S17** $^{1}$H NMR (400 MHz, DMSO-$d_6$) spectrum of **CPDC-1** activated at 473 K for 24 h under vacuum conditions showing absence of peaks corresponding to methyl benzoate.

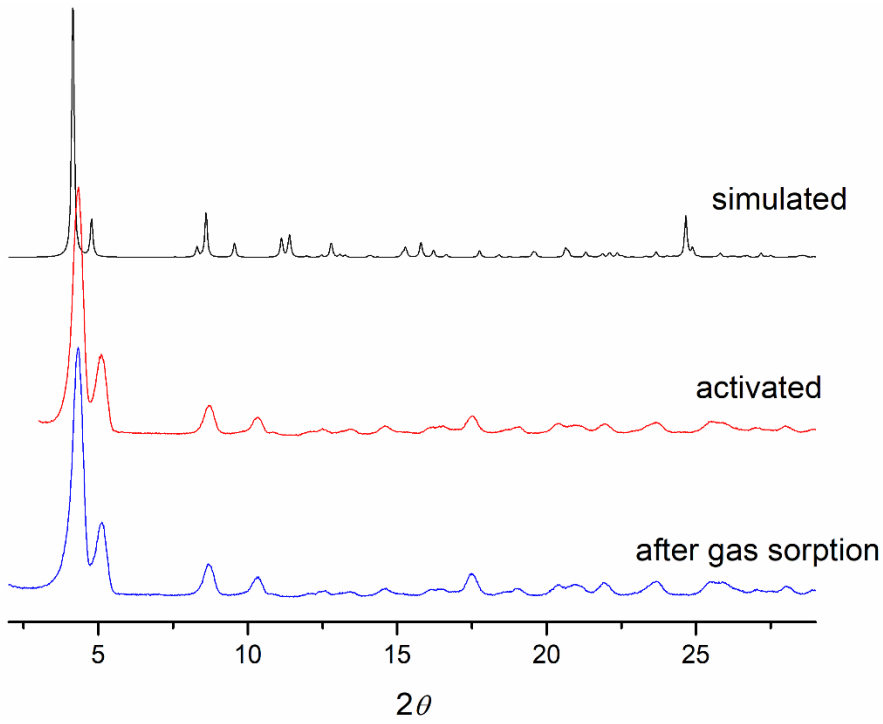



**Fig. S18** PXRD patterns of **CPDC-1**: simulated from its crystal structure containing two solvent molecules, **CPDC-1** upon activation under vacuum conditions at 473 K for 24 h, and activated **CPDC-1** after gas sorption experiment, showing no perceptible change in the framework after the experiment.

## 11. Gas sorption isotherms of activated CPDC-1

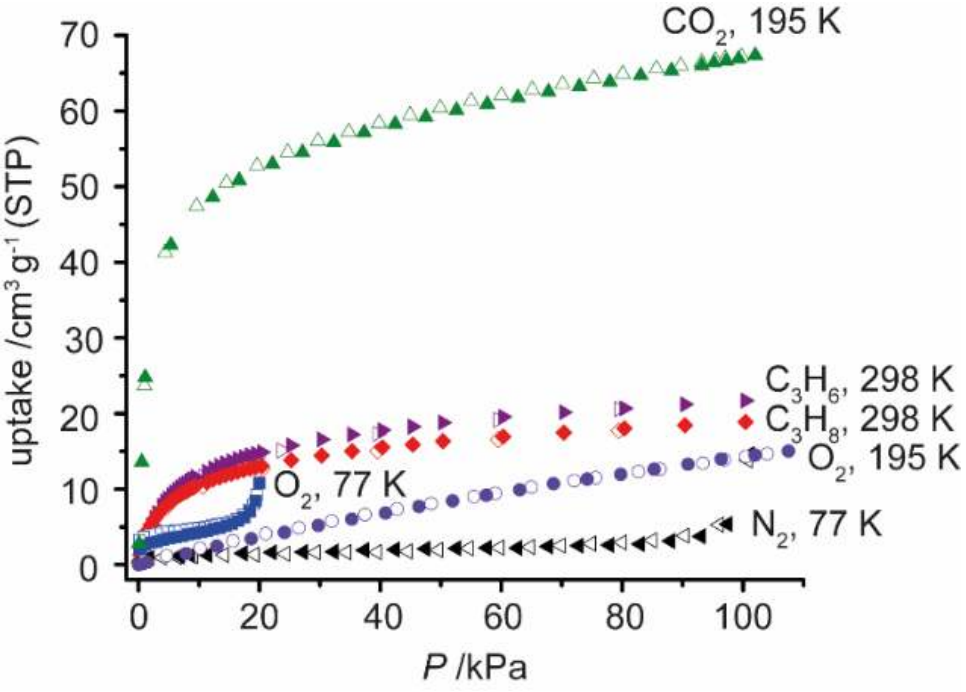



**Fig. S19** Gas sorption isotherms of activated **CPDC-1**: green triangles, $CO_2$ at 195 K; purple triangles, propene at 298 K; red squares, propane at 298 K; violet circles, $O_2$ at 195 K; blue squares, $O_2$ at 77 K and black triangles, $N_2$ at 77 K; solid symbols, adsorption and hollow symbols, desorption.

## 12. Solid-state UV-vis absorption spectrum of activated CPDC-1

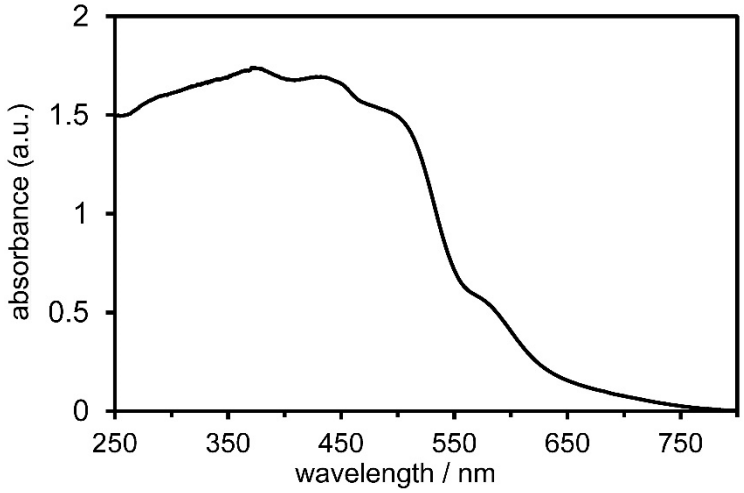



**Fig. S20** UV-vis spectra of activated **CPDC-1**.

**13. References**:


S1. G. R. Fulmer, A. J. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

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