

# Fluorescent molecular systems based on carborane- perylene-diimide conjugates

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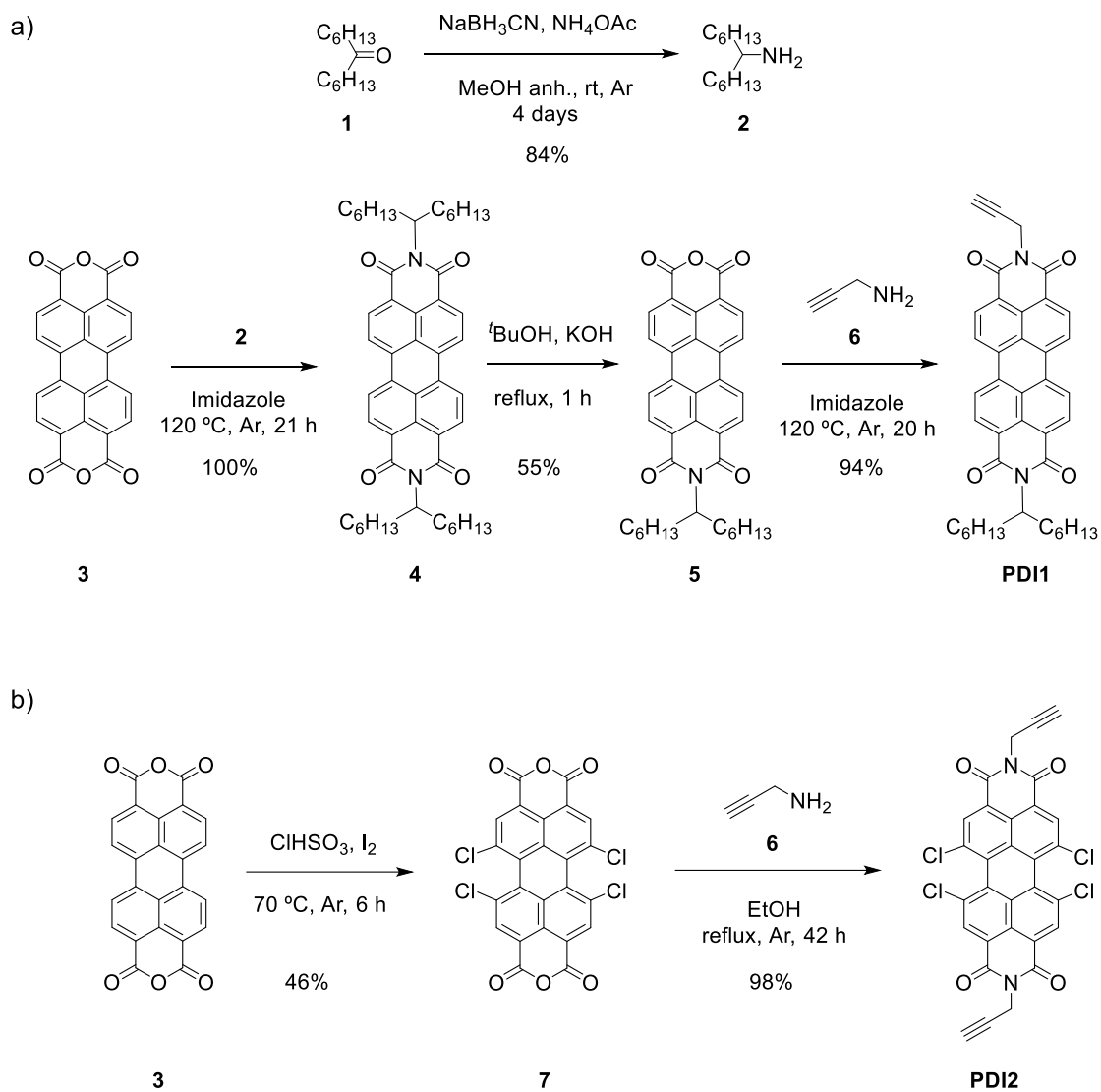
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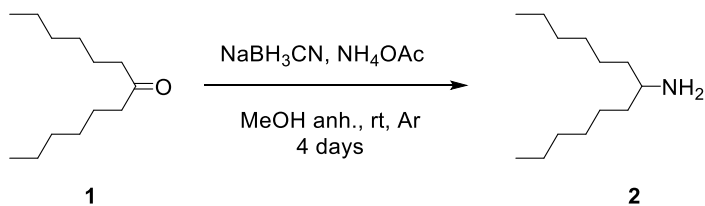
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# 1. SYNTHESIS OF PDI1 AND PDI2



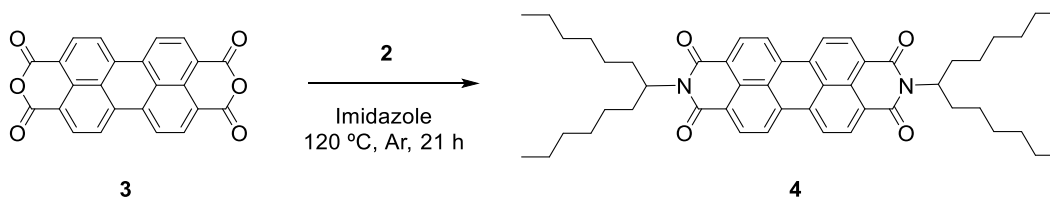
**Scheme S1.** Synthesis of (a) **PDI1** and (b) **PDI2** from perylene dianhydride **3**.

## 1.1. Synthesis of 7-tridecanamine, **2**<sup>1</sup>



7-tridecanone (**1**, 4.808 g, 24.24 mmol), NH<sub>4</sub>OAc (19.638 g, 254.74 mmol) and NaBH<sub>3</sub>CN (1.477 g, 23.50 mmol) were dissolved in 60 mL of anhydrous methanol in a 100 mL Schlenk. The mixture was stirred at room temperature under argon atmosphere for 4 days. The evolution of the reaction was monitored by TLC using chloroform as an eluent. A *p*-anisaldehyde solution was used as a staining reagent. After 4 days, basification of the reaction mixture - from pH 7 to pH 10 - was done by addition of a saturated solution of NaOH in methanol. The resulting mixture was extracted with chloroform and the organic phase was concentrated under vacuum. The resulting oil was purified by flash column chromatography (CHCl<sub>3</sub> with 2% NEt<sub>3</sub> followed by an increasing gradient of MeOH:CHCl<sub>3</sub> up to 5:95 v/v). Pure 7-tridecanamine **2** was isolated as a yellow oil (4.044 g, 84 % yield). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>, δ) 2.70 (s, 1H), 1.46 – 1.19 (m, 20H), 0.90 (m, 6H) ppm.

## 1.2. Synthesis of *N,N'*-bis(1-hexylheptyl)perylene-3,4:9,10-tetracarboxydiimide, PDI1<sup>2</sup>

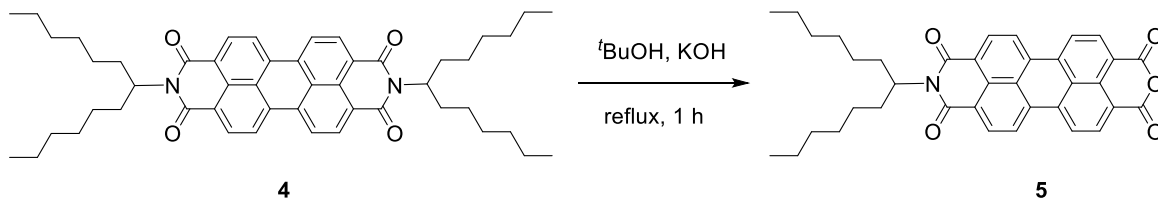


Perylene dianhydride **3** (0.867 g, 2.21 mmol), amine **2** (2.695 g, 13.5 mmol) and imidazole (8.5 g) were heated at 120 °C for 21 hours under argon atmosphere. The reaction was stopped when the starting material was consumed according to TLC. The reaction was cooled down to room temperature and acidified – from pH 9 to pH 2 – by adding a 2 M HCl solution in ethanol. The mixture turned from a dark red to a brownish-dark color and it was filtered under vacuum – for 1 hour by using a 0.2 μm Nylon filter. The filtered light red solid was dried under vacuum at 120 °C for 3 h to obtain compound **4** as a dark red solid (1.668 g, 100% yield). <sup>1</sup>H NMR (360 MHz,

$\text{CDCl}_3$ ,  $\delta$ ) 8.77–8.59 (m, 8H), 5.20 (m, 2H), 2.27 (m, 4H), 1.89 (m, 4H), 1.45-1.16 (m, 32H), 0.85 (t,  $J = 6.7$  Hz, 12H) ppm.

### 1.3. Synthesis of *N*-(1-hexylheptyl)perylene-3,4:9,10-tetracarboxil-3,4-anhydride-9,10-imide,

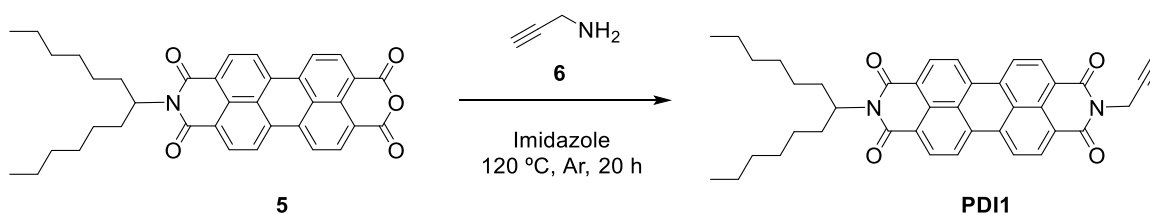
**5**<sup>3</sup>



The symmetrically functionalized perylendiimide **4** (1.805 g, 2.39 mmol) and KOH (0.485 g, 8.65 mmol) were dissolved in 48 mL of *tert*-butanol in a three-necked flask. The dark red mixture was stirred and heated under reflux for 1 hour while following the reaction by TLC. The reaction mixture was cooled down to room temperature and acidified to pH 3 by the addition of 40 mL of concentrated acetic acid and 20 mL of a 2 M aqueous HCl solution causing the appearance of a reddish-brownish clay. The mixture was filtered under vacuum by using a 0.45  $\mu\text{m}$  Nylon filter. The filtered brown solid was dried under vacuum at 120 °C for 3 hours. The solid was added to 60 mL of a 10 % aqueous solution of  $\text{K}_2\text{CO}_3$  and heated under reflux for 50 min. The resulting dark-green solution was filtered under vacuum by using a 0.45  $\mu\text{m}$  Nylon filter. The filtered brown-red solid was washed with a hot 10 % aqueous solution of  $\text{K}_2\text{CO}_3$  until the green colour of the filtrate disappeared. Straightaway, it was acidified by the addition of a 2 M aqueous HCl solution – from pH 12 to pH 2. The solid was washed thoroughly with distilled water and finally dried under vacuum at 130 °C for 5 hours. A dark red-brown solid was obtained. The dried solid was then suspended in 62 mL of distilled boiling water and 2.45 mL of  $\text{NEt}_3$ . The mixture was stirred until the solution turned red. A hot filtration under vacuum – by using paper filter for some hours – was

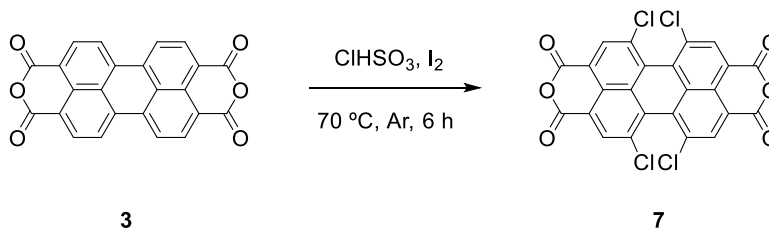
carried out. The filtered solid was washed with a 6 M aqueous HCl solution – to pH 1 – followed by rinsing with distilled water – to pH 5-6. The filtered solid was dried under vacuum at 120 °C for 4 hours to obtain **5** as a dark red solid (0.754 g, 55% yield). <sup>1</sup>H NMR (360 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80 °C, δ): 8.77 - 8.65 (m, 8H), 5.19 (tt, *J* = 8.9, 6.0 Hz, 1H), 2.26 (m, 2H), 1.95 (m, 2H), 1.46 - 1.23 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 6H) ppm.

#### 1.4. Synthesis of *N*-(1-hexylheptyl)-*N'*-propargylperylene-3,4:9,10-tetracarboxdiimide, **PDI1**<sup>4</sup>



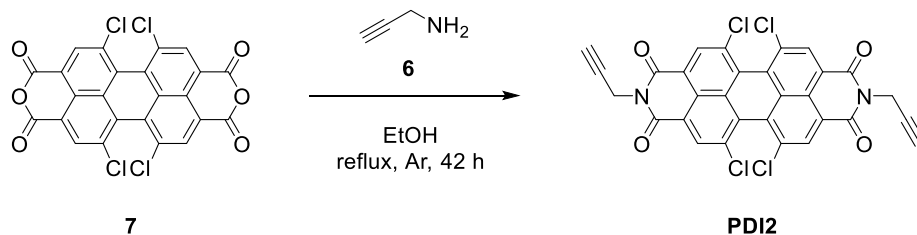
The asymmetrically functionalized monoimide **5** (0.101 g, 0.18 mmol) and imidazole (0.314 g) were dried in the Schlenk line. Propargylamine (**6**, 100 μL, 1.57 mmol) was added with a syringe under argon atmosphere and the resulting mixture was heated at 120 °C for 20 hours. The reaction mixture was cooled down to room temperature and dissolved in CHCl<sub>3</sub>. The solution was moved into a round-bottom flask where Celite (0.5 g) was added. The mixture was concentrated under vacuum getting the dry loading that was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>, followed by an increasing gradient of CH<sub>2</sub>Cl<sub>2</sub>/MeOH up to 95:5 v/v). Pure asymmetrically functionalized **PDI1** was isolated as a red solid (0.103 g, 94% yield). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>, δ) 8.72 – 8.34 (m, 8H), 5.18 (m, 1H), 4.96 (d, *J* = 2.1 Hz, 2H), 2.34 – 2.15 (overlapping m and t, 3H), 1.98 – 1.79 (m, 2H), 1.42 – 1.16 (m, 16H), 0.83 (t, *J* = 6.7 Hz, 6H) ppm.

### 1.5. Synthesis of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic, **7**<sup>5</sup>



Perylene dianhydride **3** (5.000 g, 12.75 mmol), I<sub>2</sub> (0.967 g, 3.8 mmol) and ClHSO<sub>3</sub> (34 mL, 511.52 mmol) were heated at 70 °C for 6 hours under argon atmosphere. The reaction was followed by <sup>1</sup>H NMR spectroscopy. The resulting black mixture was cooled down to room temperature and poured on 200 mL of ice. The resulting red sample was filtered under vacuum and purified by consecutive Soxhlet extractions with refluxing CH<sub>2</sub>Cl<sub>2</sub>. The filtered organic solvent was concentrated under vacuum to obtain an orange solid (3.444 g) that we found to be composed of a 9:1 mixture of the desired compound **7** (46% yield) and of the pentachlorinated derivative of **3**. Because of the low solubilities of these compounds, they could not be separated by flash column chromatography, while attempts to resolve their mixture by Soxhlet extraction were not fully successful. For this reason, compound **7** was used without further purification for the synthesis of PDI2, which did not prevent obtaining this product in good yield and high purity (see below). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>, δ) 8.80 (s) ppm.

### 1.6. Synthesis of *N,N'*-bispropargyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic diimide, **PDI2**<sup>6</sup>



The tetrachlorinated perylene core **7** (0.330 g, 0.62 mmol) and amine **6** (0.6  $\mu$ L, 9.42 mmol) were dissolved in 10 mL of EtOH and heated under reflux for 42 hours under argon atmosphere. The reaction mixture was cooled down to room temperature and the solvent was removed under vacuum. The remaining precipitate was stirred with diethyl ether and filtered. The filtered solid was dried under vacuum at 120  $^{\circ}$ C for 4 hours to obtain **2** as a dark solid (0.367 g, 98% yield). <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>,  $\delta$ ) 8.73 (s, 4H), 5.00 (s, 4H), 2.23 (s, 2H) ppm.

**Table S1.** Different reactions conditions attempted to obtain **PDI-CB1** from **PDI1** and B<sub>10</sub>H<sub>14</sub>.<sup>a</sup>

Entry	Heating conditions	Reaction time (h)	Yield (%)
1	microwave at 60 $^{\circ}$ C	4	-
2	reflux	17	15
3	reflux	72	43

<sup>a</sup> Common conditions: **PDI1**, B<sub>10</sub>H<sub>14</sub>, AgNO<sub>3</sub> cat., CH<sub>3</sub>CN/toluene, N<sub>2</sub> (see Scheme 1 in the main text).

## 2. OPTICAL PROPERTIES IN SOLUTION

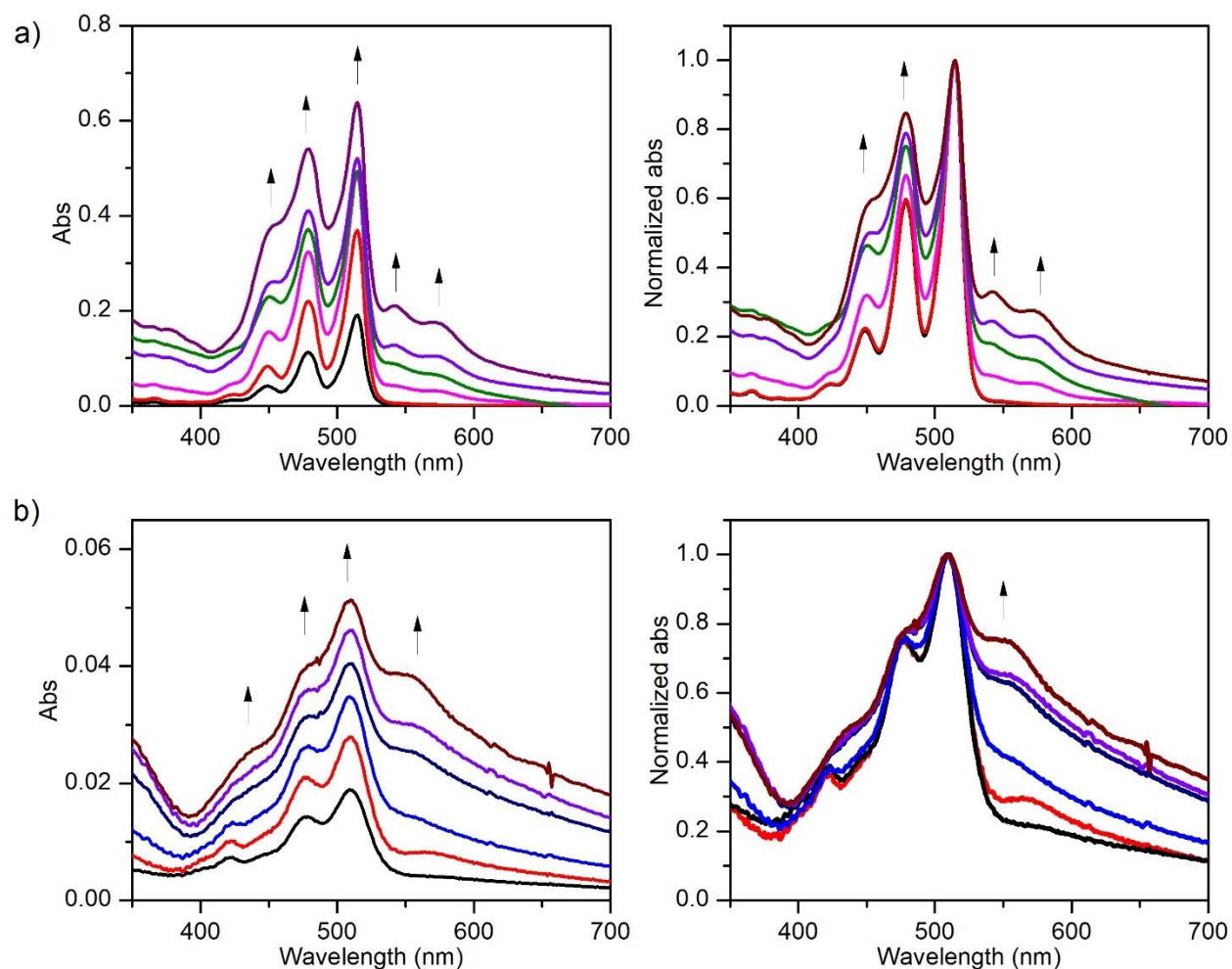
**Table S2.** Optical properties of **PDI1**, **PDI2**, **PDI-CB1** and **PDI-CB2** in acetonitrile solution.

Compound	$\lambda_{\text{abs}}^{\text{max}}$ (nm) [ $\epsilon$ ( $10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ )] <sup>a</sup>	$\lambda_{\text{f}}^{\text{max}}$ (nm) <sup>b</sup>
<b>PDI1</b>	455 [15.4], 485 [42.2], 520 [67.3]	530, 569
<b>PDI-CB1</b>	457 [15.4], 487 [40.1], 522 [64.3]	535, 574
<b>PDI2</b>	423 [9.7], 482 [25.2], 514 [35.4]	546
<b>PDI-CB2</b>	426 [8.7], 486 [23.6], 519 [33.0]	552

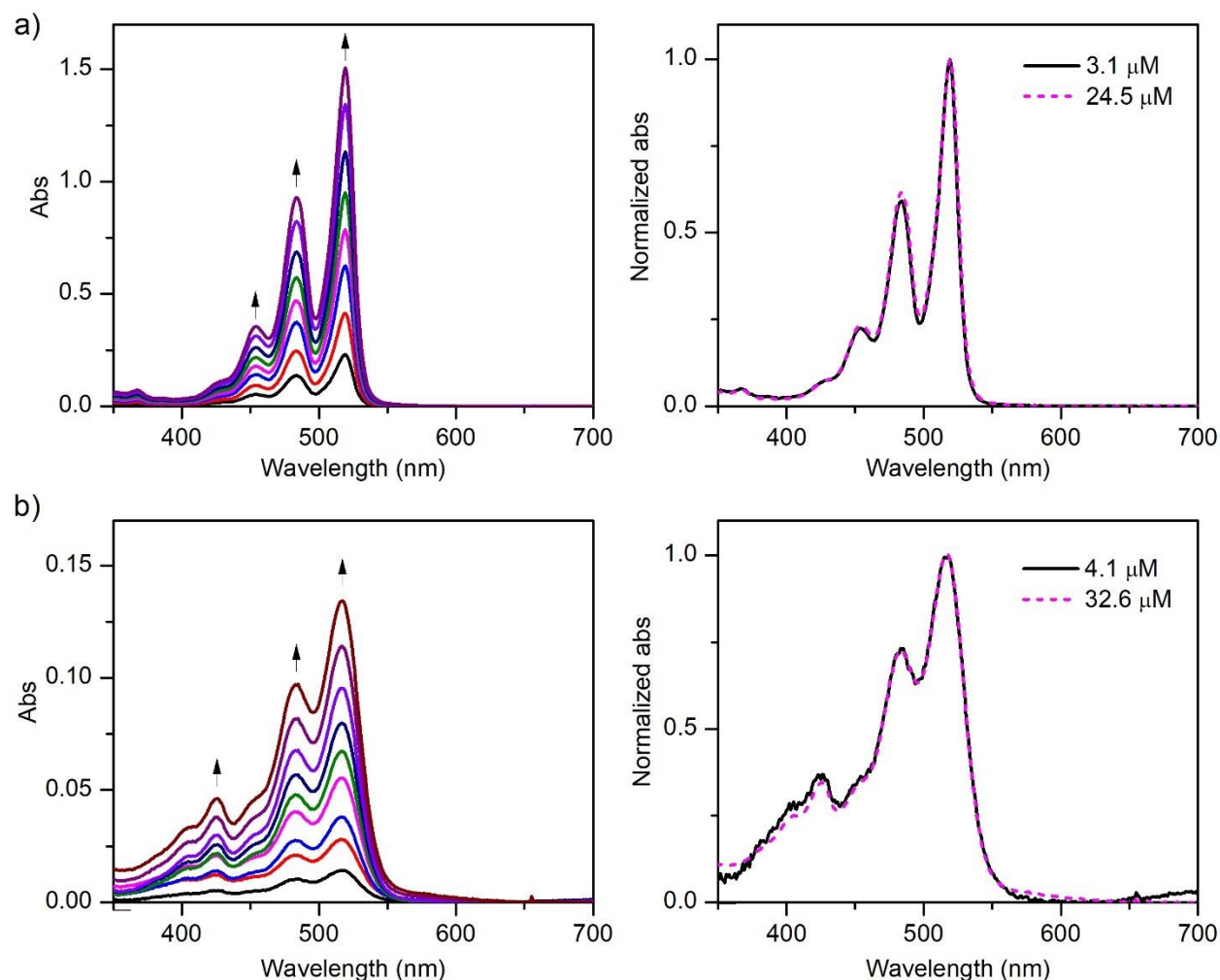
<sup>a</sup> Absorption maxima and molar absorption coefficients of the spectral vibronic peaks. <sup>b</sup> Emission maxima of the spectral vibronic peaks.



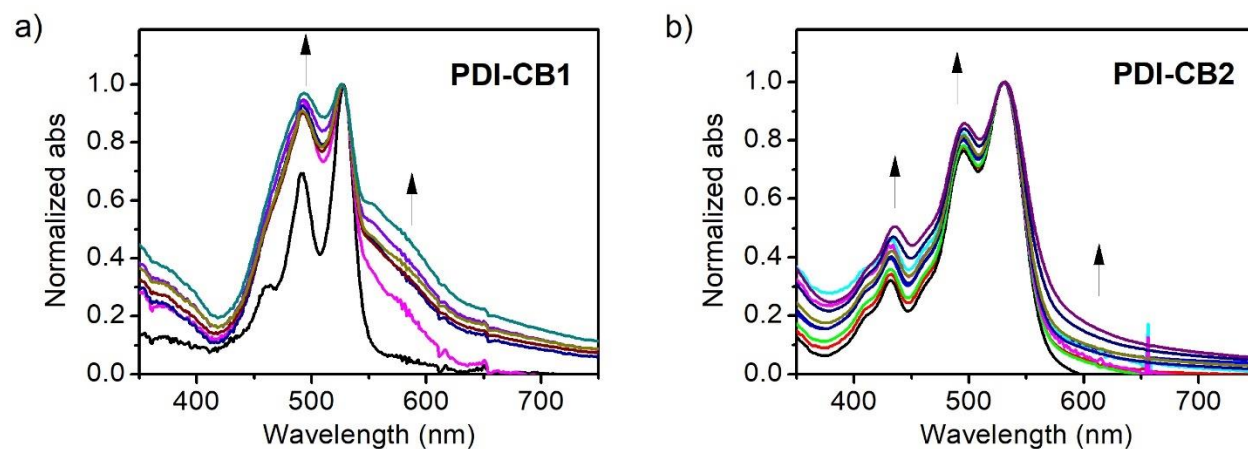
### 3. AGGREGATION STUDIES IN SOLUTION



**Fig. S1** Variation of the absorption spectra of PDI reference compounds (a) **PDI1** and (b) **PDI2** when increasing their concentration in hexane. For each compound, the variation of both the absolute (left) and normalized (right) absorbance are shown. (a) Consecutive additions of 5  $\mu\text{L}$  of a stock solution of **PDI1** in  $\text{CHCl}_3$  ( $c = 1.1 \cdot 10^{-3} \text{ M}$ ) to 2 mL of hexane in a 1 cm-thick cuvette ( $v = 5, 10, 15, 20, 25$  and  $30 \mu\text{L}$ ). (b) Consecutive additions of 5  $\mu\text{L}$  of a stock solution of **PDI2** in  $\text{CHCl}_3$  ( $c = 0.3 \cdot 10^{-3} \text{ M}$ ) to 300  $\mu\text{L}$  of hexane in a 1 mm-thick cuvette ( $v = 5, 10, 15, 20, 25$  and  $30 \mu\text{L}$ ). In all the graphs arrows indicate the direction of the spectral changes observed upon consecutive additions of **PDI1** or **PDI2**.



**Fig. S2** Variation of the absorption spectra of (a) **PDI-CB1** and (b) **PDI-CB2** when increasing their concentration in hexane. For each compound, we show: (left) the variation of the absolute absorbance (arrows indicate the direction of the spectral changes upon increasing concentrations); and (right) the normalized absorbance for the lowest and highest concentrations analyzed. (a) Consecutive additions of 5  $\mu\text{L}$  of a stock solution of **PDI-CB1** in  $\text{CHCl}_3$  ( $c = 1.25 \cdot 10^{-3} \text{ M}$ ) to 2 mL of hexane in a 1 cm-thick cuvette ( $v = 5, 10, 15, 20, 25, 30, 35$  and  $40 \mu\text{L}$ ). (b) Consecutive additions of 5  $\mu\text{L}$  of a stock solution of **PDI-CB2** in  $\text{CHCl}_3$  ( $c = 0.25 \cdot 10^{-3} \text{ M}$ ) to 300  $\mu\text{L}$  of hexane in a 1 mm-thick cuvette ( $v = 5, 10, 15, 20, 25, 30, 35, 40$  and  $45 \mu\text{L}$ ).



**Fig. S3** Variation of the normalized absorption spectrum of (a) **PDI-CB1** and (b) **PDI-CB2** upon consecutive additions of: 5  $\mu\text{L}$  of a stock solution of **PDI-CB1** in dioxane ( $c = 0.4 \cdot 10^{-3} \text{ M}$ ) to 2 mL of a 3:2 dioxane:water mixture ( $v = 5, 10, 15, 20, 25, 30$  and  $35 \mu\text{L}$ ); and 15  $\mu\text{L}$  of a stock solution of **PDI-CB2** in dioxane ( $c = 0.4 \cdot 10^{-3} \text{ M}$ ) to 2 mL of a 2:3 dioxane:water mixture ( $v = 15, 30, 45, 60, 75, 90, 105, 120, 135$  and  $150 \mu\text{L}$ ).

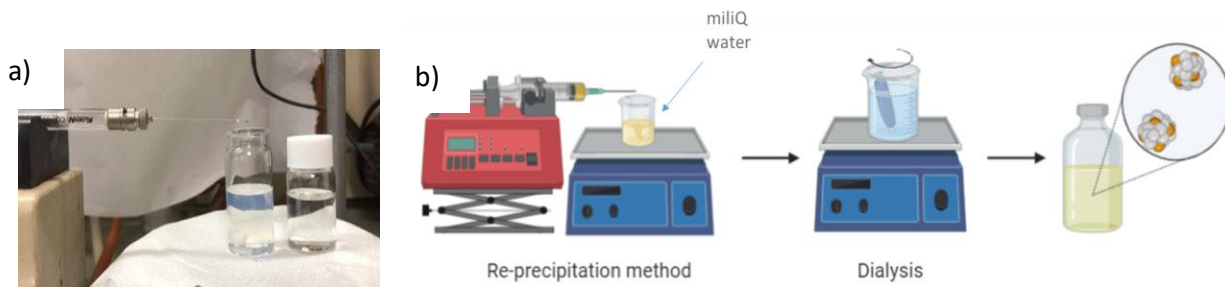


**Fig. S4** Images of the emission ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ) from nonaggregated and aggregated samples of: (a) **PDI1** in  $\text{CHCl}_3$  (left) and hexane (right); (b) **PDI2** in  $\text{CHCl}_3$  (left) and hexane (right); (c) **PDI-CB1** in dioxane (left) and water (right); (d) **PDI-CB2** in dioxane (left) and water (right).

## 4. PREPARATION AND CHARACTERIZATION OF NANOSTRUCTURES

### 4.1. Preparation of PDI-CB1 nanoparticles

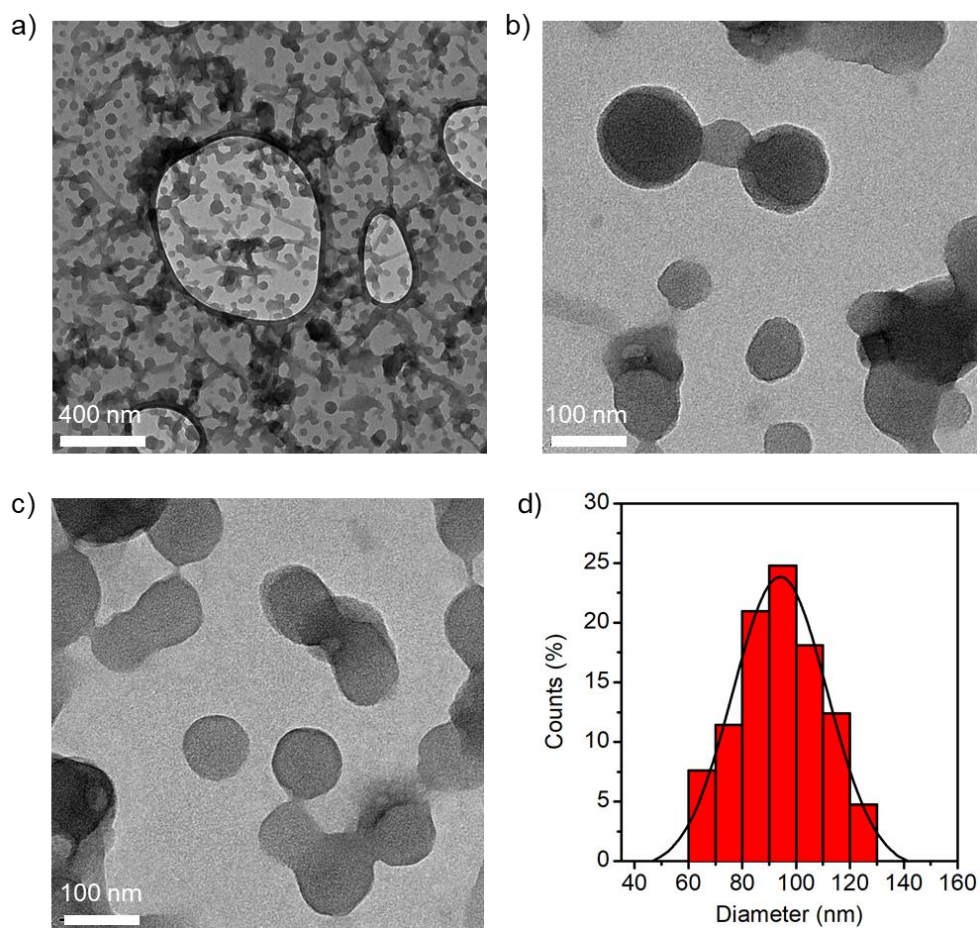
The re-precipitation method is a single-step self-assembly method for obtaining organic nanoparticles. It is the most popularly used solvent-exchange process that has been developed over a decade by several research groups such as Nakanishi's, Majima's, Yao's, Park's, Barbara's, Horn and co-workers. These various groups have successfully investigated the preparation, size distribution and dependency of the luminescence and emission enhancement of numerous organic nanoparticles.<sup>7,8</sup> Some of the crystalline nanoparticles obtained by these groups have confirmed the formation of J-aggregates which results in enhanced radiative decay rate.<sup>9</sup> The re-precipitation method generally consists of adding 1 mL of concentrated solution ( $10^{-3}$  M in this case) of a water miscible organic solvent solution (tetrahydrofuran, THF) of a hydrophobic compound (**PDI-CB1**) in 9 mL of milliQ water at the rate of 1 mL/hour, and stirred vigorously at 400 rpm. The fast mixing of the two solvents induces the precipitation of the organic compound in micro- to nanosized aggregates since the organic molecules get saturated in the new solvent mixture (Fig. S4). After an hour of continuous stirring, the mixture was kept stirring for another hour, even after the completion of the addition of THF. Gradually, precipitation in the solution mixture appeared and the solubility of the organic material decreased thus these molecules aggregated homogeneously and formed nanoparticles.<sup>10</sup> The final concentration prepared was  $10^{-4}$  M.



**Fig. S5** (a) Preparation of **PDI-CB1** NPs: an aqueous solution turns turbid as **PDI-CB1** dissolved in THF is added dropwise. (b) Schematic representation of the reprecipitation method followed by dialysis.

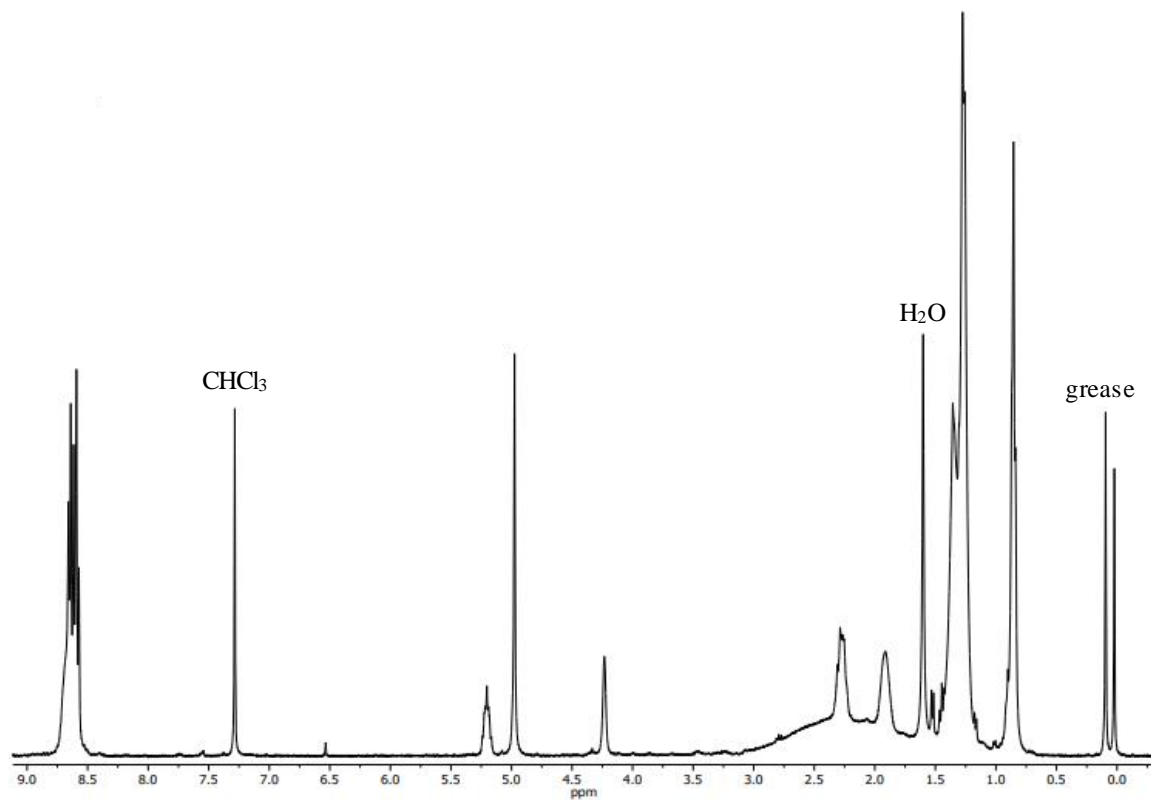
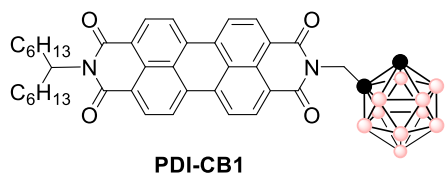
The experimental parameters involved in the preparation technique to control the particle size are temperature, concentrations, volume and velocity of the syringe, nature, and volume of the miscible solvent, as well as the composition, time, and agitation speed (rpm) of the non-solvent. Hence, for the growth of organic nanoparticles both kinetics and thermodynamics processes are being considered.<sup>11</sup> To obtain a NP suspension only in water, the THF was removed with a dialysis procedure using a D9652-100FT dialysis tubing cellulose membrane. Dialysis was done using a 500 mL beaker containing milliQ water, and water was changed every 6 hours during the entire duration of 72 hours.

## 4.2. Characterization of PDI-CB1\_NP

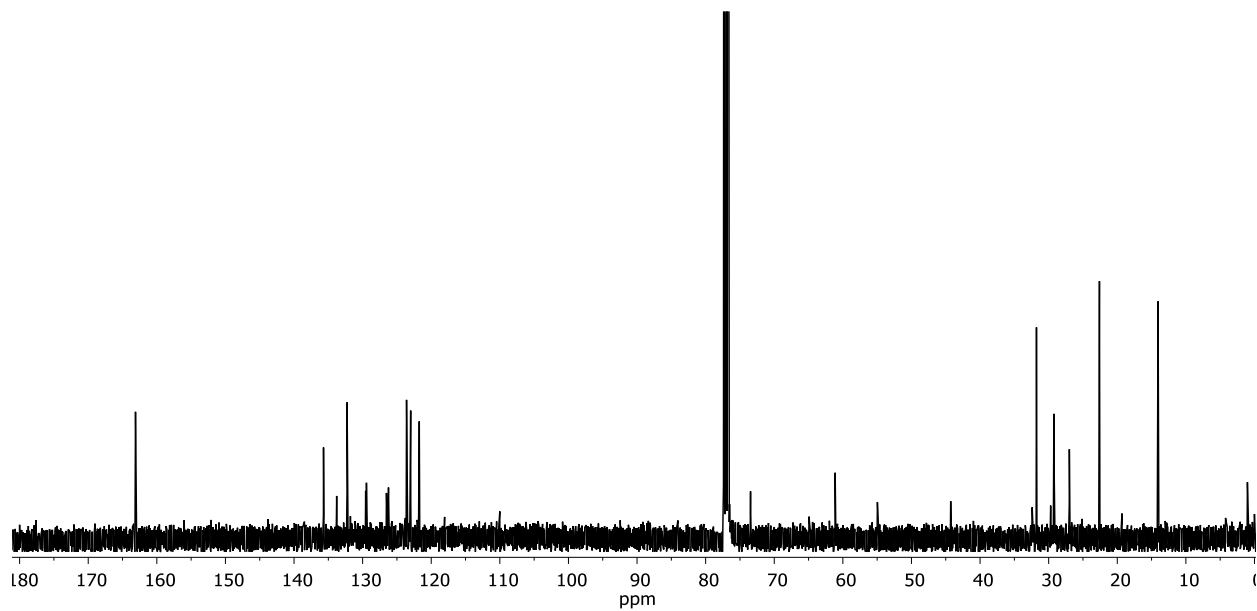


**Fig. S6** (a-c) TEM images of **PDI-CB1\_NP**. (d) Histogram of **PDI-CB1\_NP** diameters measured for 100 nanoparticles by TEM (average diameter =  $95 \pm 10$  nm).

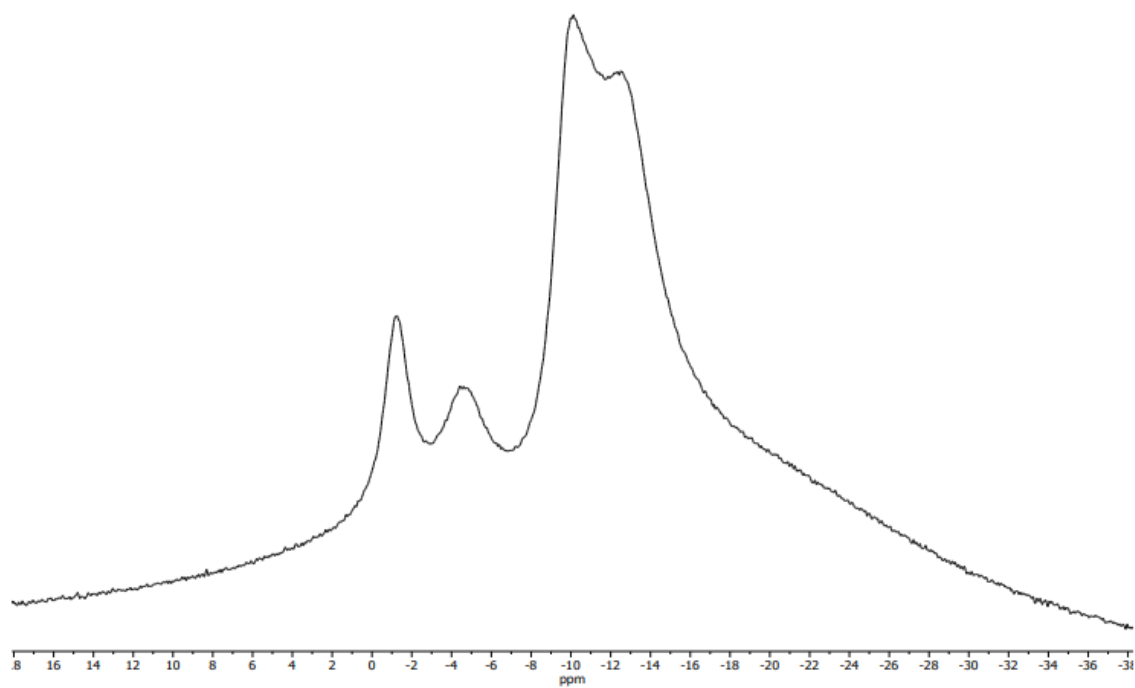
## 5. $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ , $^{11}\text{B}\{^1\text{H}\}$ NMR AND IR-ATR SPECTRA OF PDI-CB1 AND PDI-CB2



**Fig. S7**  $^1\text{H}$  NMR of PDI-CB1 (250 MHz,  $\text{CDCl}_3$ )

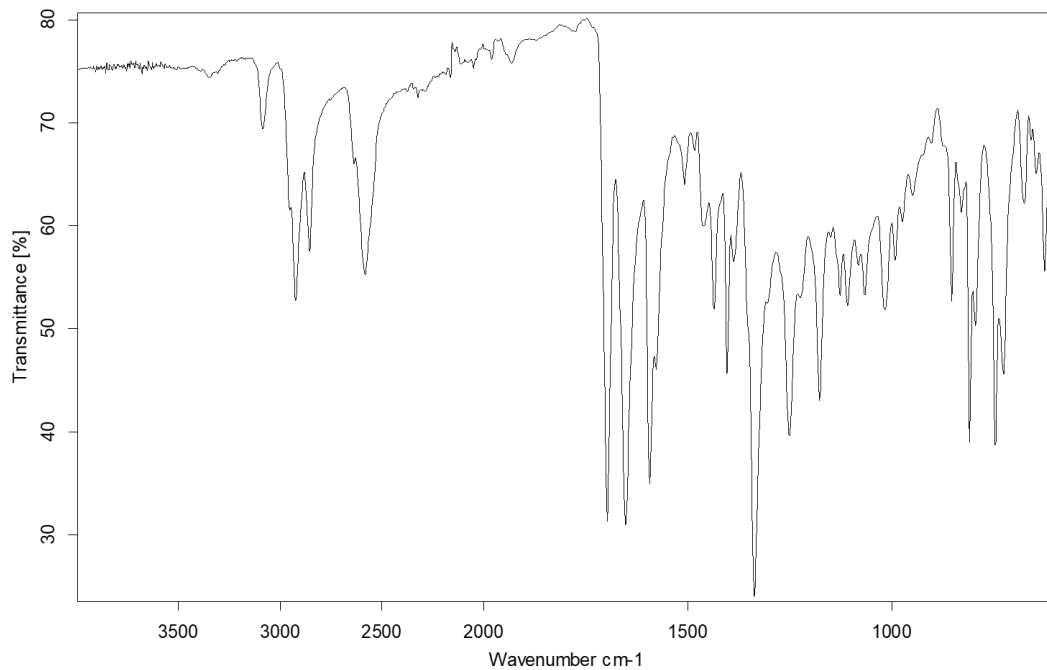


**Fig. S8**  $^{13}\text{C}\{^1\text{H}\}$  NMR of **PDI-CB1** (100 MHz,  $\text{CDCl}_3$ )

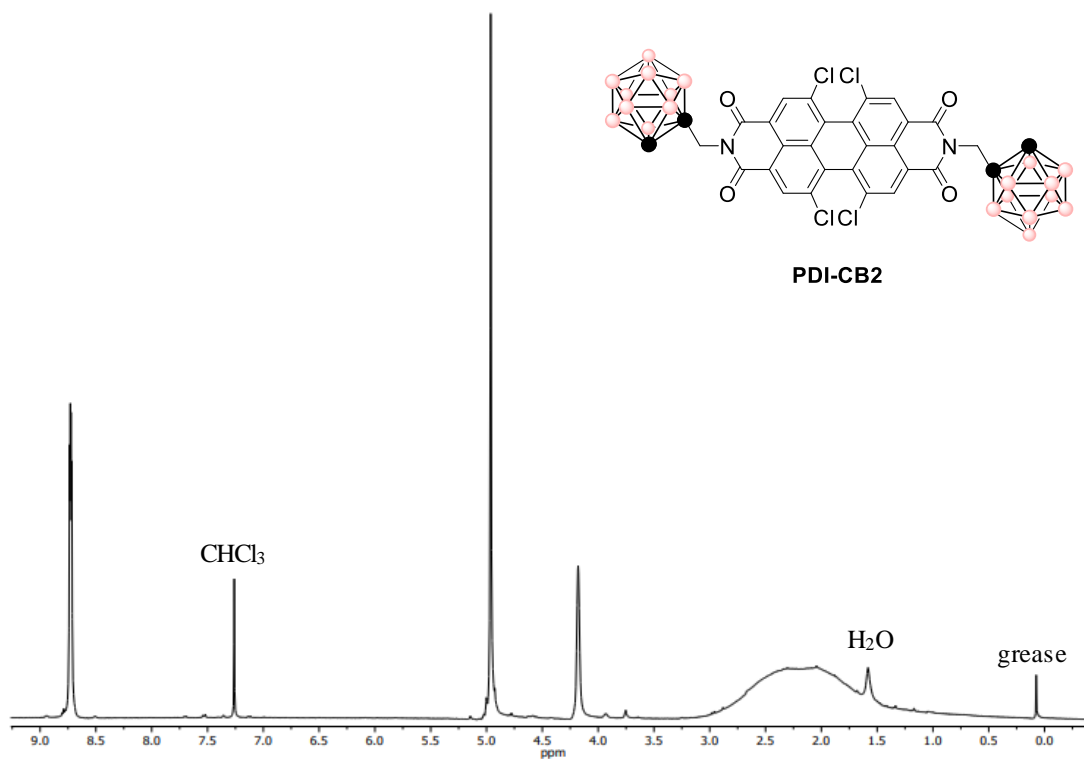


**Fig. S9**  $^{11}\text{B}\{^1\text{H}\}$  NMR of **PDI-CB1** (128 MHz,  $\text{CDCl}_3$ )

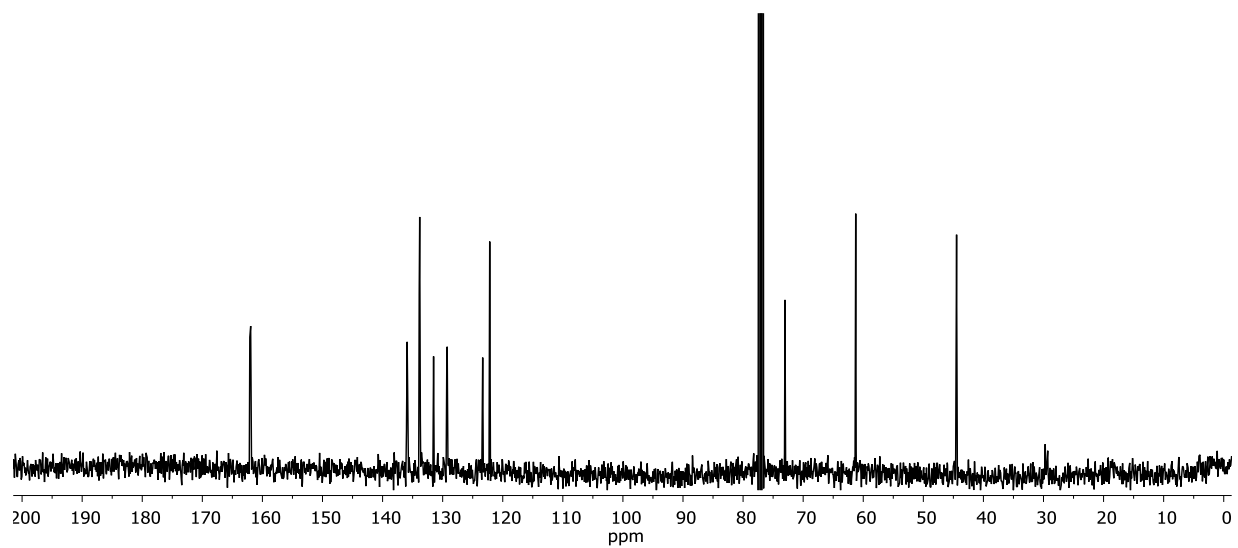




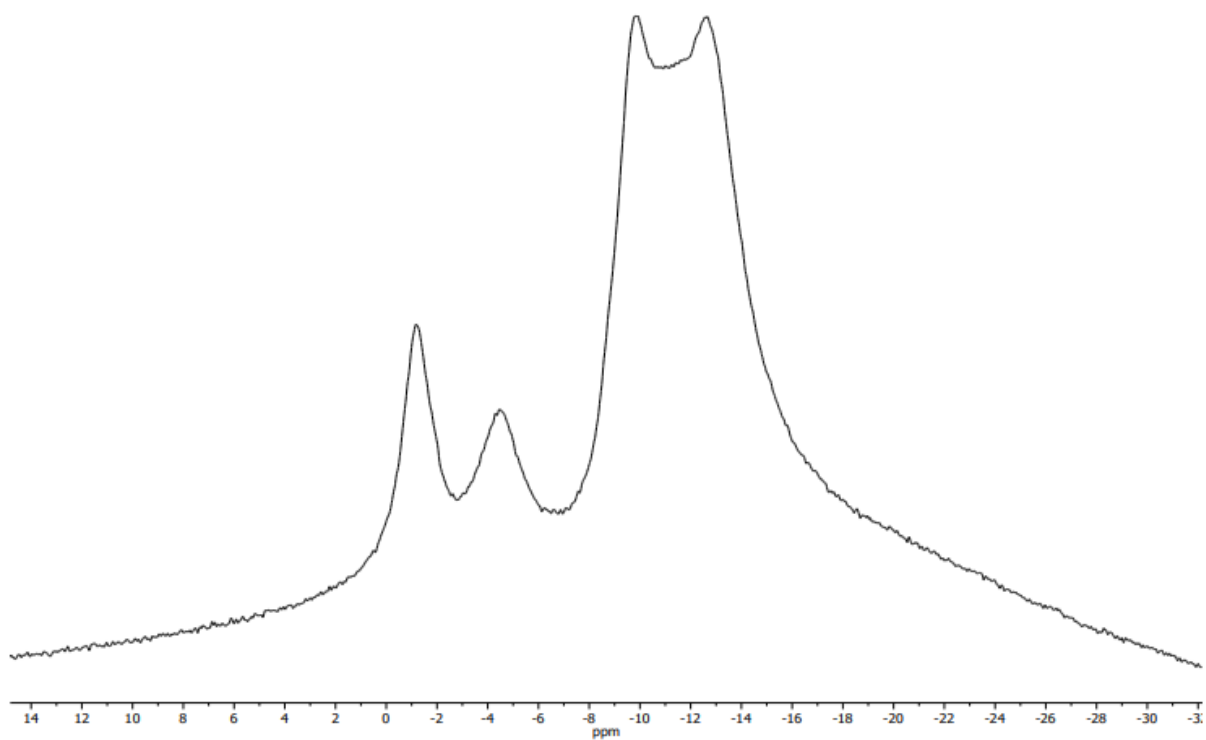
**Fig. S10** IR spectrum of **PDI-CB1** (ATR).



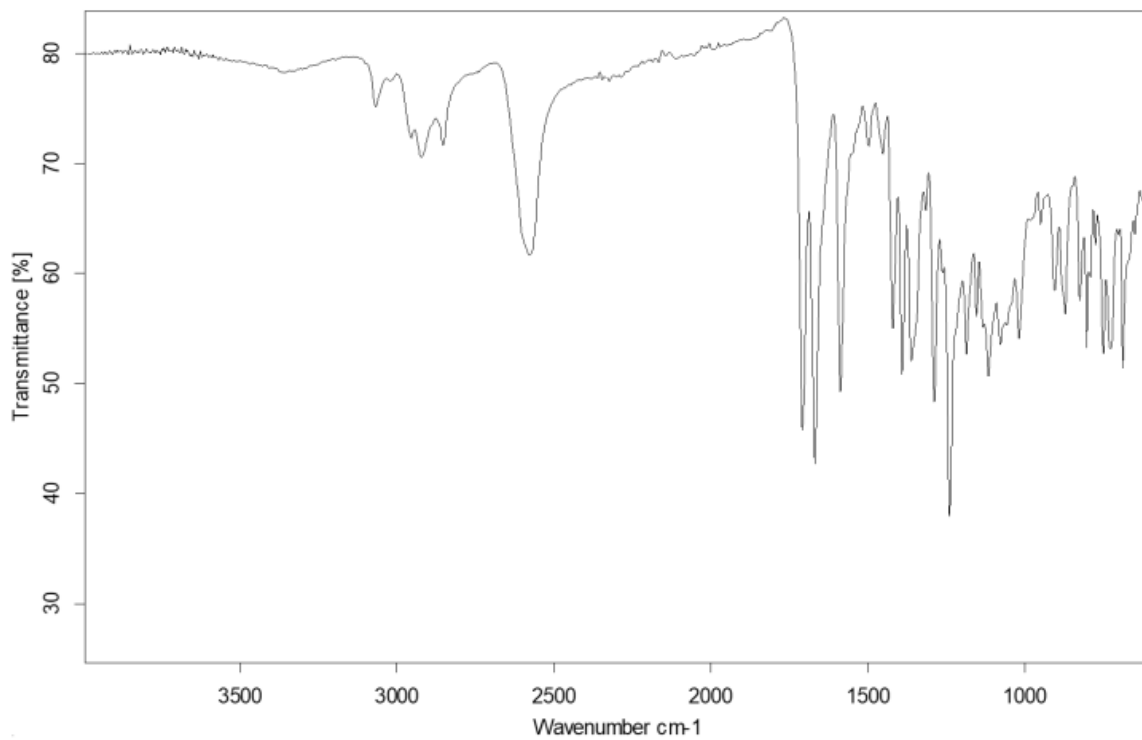
**Fig. S11** <sup>1</sup>H NMR spectrum of **PDI-CB2** (250 MHz, CDCl<sub>3</sub>)



**Fig. S12**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **PDI-CB2** (100 MHz,  $\text{CDCl}_3$ )



**Fig. S13**  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **PDI-CB2** (128 MHz,  $\text{CDCl}_3$ )



**Fig. S14** IR spectrum of **PDI-CB2** (ATR).

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