Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

From molecules in solution to molecules on surfaces – using supramolecular dyads to form functional self-assembled networks on graphene

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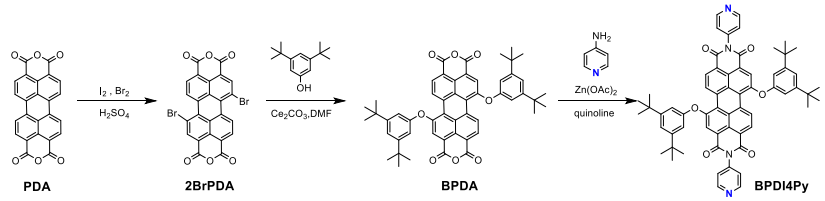
SUPPORTING INFORMATION

Synthetic protocols for the perylene components (PDA, PDIs)



Scheme S1. Synthetic route towards the 3- and 4-pyridil, bis(3,5-*t*-butylphenoxy) perylenediimides

1,7-dibromoperylene-3,4:9,10-tetracarboxydianhydride[1] (2BrPDA)

3,4:9,10-perylenetetracarboxylic dianhydride PDA (28.5 g, 72.7 mmol, 1eq.) is added to concentrated sulfuric acid (420 mL) and stirred at 55°C for a period of 24 hrs. The mixture turns into a pink-violet suspension. Iodine (0.685 g, 2.7mmol, 0.04 eq.) is then added and the mixture stirred for another hour at 55°C. Bromine (8.3 mL, 162 mmol) is then slowly added (0.14 mL/min) to the reaction mixture. After the addition is complete, the reaction is heated to 85°C for 22 h. The resulting red suspension is left to cool in an ice bath before adding cold distilled water (66mL) to fully precipitate the crude product. The red solid is filtered under vacuum, rinsed with distilled water (2 x 100 mL) and ethanol (300 mL). The crude solid is dried at 45 °C under reduced pressure for 48 h.

IR: 1818, 1768, 1736,1724, 1591, 1560, 1499, 1406, 1375, 1306, 1285, 1229, 1212, 1187, 1164, 1139 cm^{-1}

1,7-(3',5'-di-t-butylphenoxy)perylene-3,4:9,10-tetracarboxydianhydride[2] (BPDA)

2BrPDA (3.01 g, 5.45 mmol, 1eq.), 3,5-di-tert-butylphenol (3.49g, 16.9 mmol, 3.1 eq.), and caesium carbonate (3.20 g, 9.81 mmol, 1.8 eq.) were added to a 3-neck-RBF under argon. Whilst stirring, N,N-dimethylformamide (180 mL, anh.) was added via syringe and the mixture heated to 160 °C for a period of 2 h. The dark red mixture was cooled to rt, and cold acetic acid (60 mL) was added, leaving it to stir in an ice bath over a 2h period. MeOH (20mL) was added to precipitate the product as a red solid. The solid was filtered, washed with cold methanol (200mL), and purified via soxhlet with methanol (300mL, 16h) as solvent. The dark red paste recovered in the soxhlet was dried under reduced pressure (0.1 mbar) at 40 °C to give the expected product as a dark red solid (3.91 g, 72%).

1H NMR (400 MHz, Chloroform-d) 9.76 (d, 2H, J= 8.4 Hz), 8.69 (d, 2H, J= 8.4 Hz), 8.37 (s, 2H), 7.42 (s, 2H), 7.04 (s, 4H), 1.36 (s, 36H).

N, N'-di(4-pyridyl)-1,7-bis(3',5'-di-tert-butylphenoxy)perylenediimide (BPDI4Py)

The BPDA (0.10g, 0.13 mmol) is added together with 4-aminopyridine (0.41g, 0.44 mmol) and zinc acetate (0.012g, 0.07 mmol) in quinoline (5mL, dist.). The mixture is bubbled with argon for 10 min whilst stirring. It is the heated to reflux overnight whilst stirring under an inert atmosphere. The reaction is cooled to room temperature and poured onto an HCl aq. solution (2N, 30 mL), where a precipitate is formed, collected by filtration and washed thoroughly with water. The dry, crude material is purified by column chromatography using a solvent mixture of DCM/MeOH (50:1) where the product is collected as the main fraction. Re-crystallisation from dichloromethane/hexanes gives a dark red solid, 0.83g, 70% yield).

1H NMR (400 MHz, Chloroform-d) 9.76 (d, 2H, *J*= 8.0 Hz),8.78 (d, 4H, *J*= 6.3 Hz), 8.65 (d, 2H, *J*= 8.0 Hz), 8.32 (s, 2H), 7.39 (s, 2H), 7.28 (d, 4H, *J*= 6.3 Hz), 7.08 (s, 4H), 1.33 (s, 36H).

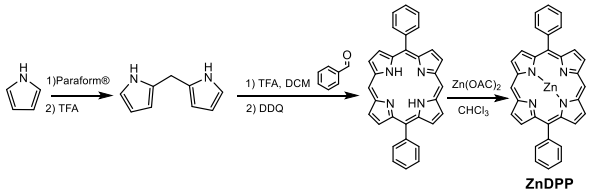
N, N'-di(*n*-heptyl)-1,7-bis(3',5'-di-tert-butylphenoxy)perylenediimide (BPDIC7)

Following same procedure as above, BPDA (0.10g, 0.13 mmol) is added together with 1-heptylamine (0.51g, 0.44 mmol) and zinc acetate (0.012g, 0.07 mmol) in quinoline (5mL, dist.).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (d, *J* = 8.4 Hz, 2H), 8.64 (d, *J* = 8.4 Hz, 2H), 8.36 (s, 2H), 7.36 (t, *J* = 1.7 Hz, 2H), 7.03 (d, *J* = 1.6 Hz, 4H), 4.20 – 4.08 (m, 4H), 1.72-1.68 (m, 4H), 1.42-1.38 (m,4H), 1.32-1. 72 (s, 36H), 1.11-0.98 (m, 8H), 0.86 (m, 4H), 0.07 (s, 6H).

Synthetic protocols for the ZnPc and ZnDPP pedestals

The 5,15-diphenyl zincporphyrin (ZnDPP) was synthesised following previously reported procedures3a,b whilst the zinc phthalocyanine (ZnPc) was commercially available from Sigma-Aldrich.



Scheme S2. Synthetic route towards the zinc diphenylporphyrin (ZnDPP).

Di(1H-pyrrol-2-yl)methane (dipyrromethane)[3a,b]

Paraformaldehyde (0.77 g, 25 mmol, 1 eq.) and pyrrole (175 mL, 2.5 mol, 100 eq.) were added to a 500 mL 3-neck-RBF under inert atmosphere. Whilst stirring, the suspension was heated to 55 °C for 3 h to partially solubilized the paraformaldehyde. The mixture was cooled at rt and TFA was slowly added via syringe. The mixture was stirred for 1 h and the color passed from pale yellow to pale orange. NaOH was added and the mixture stirred 45 further minutes at rt. The pyrrole was evaporated under reduced pressure and the crude purified by flash chromatography. The gradient used was PE-DCM from 10:0 to 8:2 over 5 CV, the product was the second fraction collected. After evaporation under reduced pressure, the product was obtained as an off-white powder (1,65 g, 44%).

1H RMN (300 MHz, Chloroform-d) 7,89 (s, 2H) ; 6,67 (s, 2H) ; 6,16 (t, J = 3 Hz, 2H) ; 6,04 (s, 2H) ; 4,00 (s, 2H)

Diphenylporphyrin (DPP)[3a,b]

Dipyrromethane (0.20 g, 1.24 mmol, 1 eq.) and benzaldehyde (0.14 mL, 1.24 mmol, 1 eq.) were added to a 1 L RBF containing DCM (500 mL, degassed). TFA (0.20 mL, 2.28 mmol, 2 eq.) was slowly added via syringe and the mixture was stirred at 25 °C for 1 h. DDQ was added (0.55 g, 2.28 mmol, 2 eq.) and the mixture stirred at 25 °C for 16 h. Triethylamine (5 mL) was slowly added and the reaction left to stir for 5 minutes. The solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography. The gradient used was cyclohexane-DCM from 10:0 to 5:5 over 4 CV. The DPP was obtained as a purple solid (174 mg, 29%) after evaporating the fraction collected.

1H RMN (300 MHz, CDCl3) : δ (ppm) = 10,32 (s, 2H) ; 9,41 - 9,39 (d, 4H) ; 9,10 - 9,08 (d, 4H) ; 8,30 – 8,27 (dd, 4H) ; 7,83 – 7,80 (m, 6H) ; -3,1 (s, 2H)

Zinc diphenylporphyrin (ZnDPP) 3a,b

Diphenyl porphyrin (0.50 g, 1,1 mmol, 1 eq.) was solubilized in chloroform (150 mL) in 3-neck-RBF. Whilst stirring, the solution was bubbled with argon for 20 min and Zn(OAc)2 (2.2 g, 12 mmol, 12 eq.) were added. The stirring mixture was heated to reflux for 20 h. After cooling to rt, the crude solution was filtered through a silica plug and eluted with chloroform. The solvent was evaporated under reduced pressure to give ZnDPP as purple crystalline solid (545 mg, 96%).

1H NMR (600 MHz, CDCl3) 10.35 (s, 2H), 9.46 (d, J = 4.4 Hz, 4H), 9.16 (d, J = 4.5 Hz, 4H), 8.28 (d, J = 6.8 Hz, 4H), 7.83 – 7.78 (m, 6H). λmax (CHCl3): 407 nm, 535 nm

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1. Würthner, F.; Stepanenko, V.; Chen, Z.; Saha-Möller, C. R.; Kocher, N.; Stalke, *J. Org. Chem.* **2004**, *69* (23), 7933–7939.
2. Ahrens, M. J.; Sinks, L. E.; Rybtchinski, B.; Liu, W.; Jones, B. A.; Giaimo, J. M.; Gusev, A. V.; Goshe, A. J.; Tiede, D. M.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126* (26), 8284–8294. ht
3. a) D. K. Dogutan, M. Ptaszek, J. S. Lindsey, *J. Org.Chem*.,**2007**, *72*, 5008-5011. b) J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem*., **1987**, *52*, 827.

General experimental conditions – absorbance and fluorescence experiments

Absorbance measurements were recorded on a Agilent® Cary 50 or Cary 100 spectrometer using an automatic baseline. 1 cm or 2 mm large Quartz cell were used, as specified. Volumes measured for the titration were done using a micropipette or Hamilton® syringes. The absorbance measurements were taken at room temperature in a sealed cuvette with a Teflon® cap. Absorbance measurements were also used to control the concentration of the stock solutions using the Beer-Lambert law (A=ε.l.C).Two set-ups were used for the fluorescence and lifetime studies.Emission and excitation spectra were recorded using a Varian Cary eclipse fluorescence Spectrophotometer at room temperature in a quartz cell, with a 5 nm slit and an averaging scan of 100 milliseconds. Solutions in toluene were diluted at 10-5 to 10-7 M. Confocal microfluorescence with time-correlated single photon counting analyses were performed using a homemade set-up coupling a picosecond supercontinuum laser (NKT Photonics, SuperK EVO) to an inverted optical microscope.

Absorbance Titration protocols

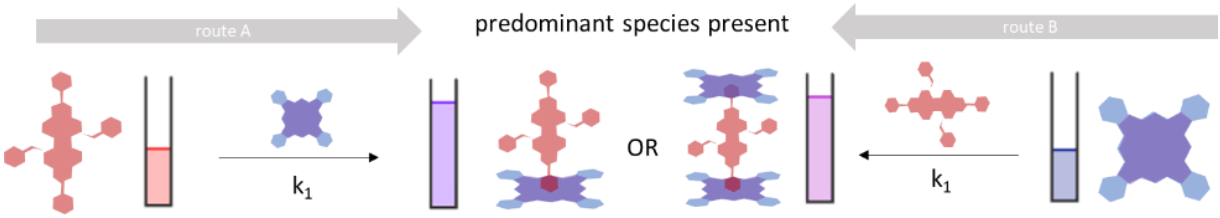


Figure S1. Representation of the two different titration experiments, changing the [H] and [G] species, and the resulting predominant dyad/triad in each case. Addition of the Zn pedestal to a PDI solution is expected to yield the 1:1 dyad, and for the reverse (PDI to Zn pedestal) , the 2:1 sandwich-type triad.

General absorbance titration protocol of BPDI4Py by ZnPc / ZnDPP (Route A)

To a BPDI4Py solution (1,4 x 10^{-6} M), 10 µL (from 10 to 100 µL) and 20 µL (from 120 to 300 µL) aliquots of ZnPc/ZnP solution in $CHCl_3$ (1.3 x 10^{-4} M) were added and the absorbance was recorded after each addition.

General absorbance titration protocol of ZnPc / ZnDPP by BPDI4Py (Route B)

To a ZnPc/ZnP solution in CHCl3 (1.6 x 10-6 M), 5 µL (from 5 to 50 µL), 10 µL (from 60 to 100 µL), 20 µL (from 120 to 200 µL) and 100 µL (300µL) aliquots of BPDI4Py solution (6.8 x 10-5 M) were added and the absorbance was recorded after each addition.

General fluorescence titration (ZnDPP-PDI4)

PDI4 (1.2 mg, 1.3µmol) was solubilized in toluene (100 mL). The solution was sonicated 10 min then left to rest 1 day before to be used as a stock solution at 13 µM. ZnDPP (2.2 mg, 4.2 µmom) was solubilized in toluene (100 mL). The solution was sonicated 10 min then left to rest 1 day before to be used as a stock solution at 42 µM. Those two solutions were used in the following titrations.

Protocol A: In a 2 mm cuvette containing 200 µL of the BPDI4Py solution were added 10 to 70 µL of ZnDPP (6 mixes) and 200 µL of toluene. Emission and lifetime were recorded at 415 nm (excitation of ZnDPP) and 515 nm (excitation of PDI4). 100 µL of the BPDI4Py solution diluted with 500 µL of toluene was used as the BPDI4Py reference. 50 µL of the ZnDPP solution in 400 µL of toluene was used as ZnDPP reference. Fluorescence lifetimes were fitted with a bi-exponential decay model.

Protocol B: In a 2 mm cuvette containing 100 µL of the PDI4 solution were added 50 to 140 µL of ZnBPP (8 mixtures) and 300 µL of toluene. Emission and lifetime were recorded at 415 nm (excitation ZnBPP) and 515 nm (excitation BPDI4Py). 100 µL of the PDI4 solution diluted with 500 µL of toluene was used as PDI4 reference. 50 µL of the ZnDPP solution in 400 µL of toluene was used as ZnDPP reference. Fluorescence lifetimes were fitted with a bi-exponential decay model.

General fluorescence titration (ZnPc-PDI4)

A 1:1 molar ratio solution of ZnPc and BPDI4Py in CHCl3 (10 µM, 5 mL) was stirred at 40 °C for 1 h. The solvent was evaporated under reduced pressure and the purple solid was solubilized in toluene (5 mL) to obtain a stock

solution. This stock solution was diluted in the UV-Vis cell to reach the µM scale targeted concentration. The concentration was monitored by absorbance measurements. The emission spectra of the solution were collected using the micro fluorescence confocal setup. The solution fluorescence emission spectra of BPDI4Py were recorded with 532 nm excitation, and the solution fluorescence emission spectra of ZnPc with a 620 nm excitation.

Characteristic absorption spectra of the molecular components in solution

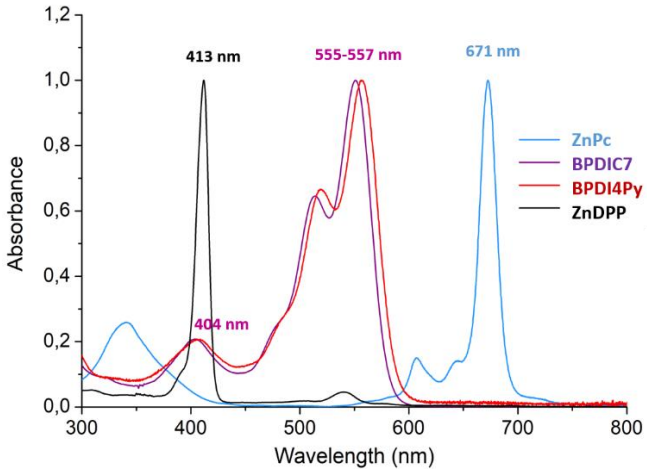


Figure S2. Normalised absorption spectra of the ZnPc, ZnDPP, BPDI4Py and BPDIC7 compounds in CHCl3, identifying the absorption wavelengths that will be monitored during the absorbance titration experiments. These spectra were also used to determine the excitation wavelengths for the subsequent fluorescence experiments.

Reverse absorbance titration (ZnPc and ZnDPP to BPDI4Py) in $CHCl_3$

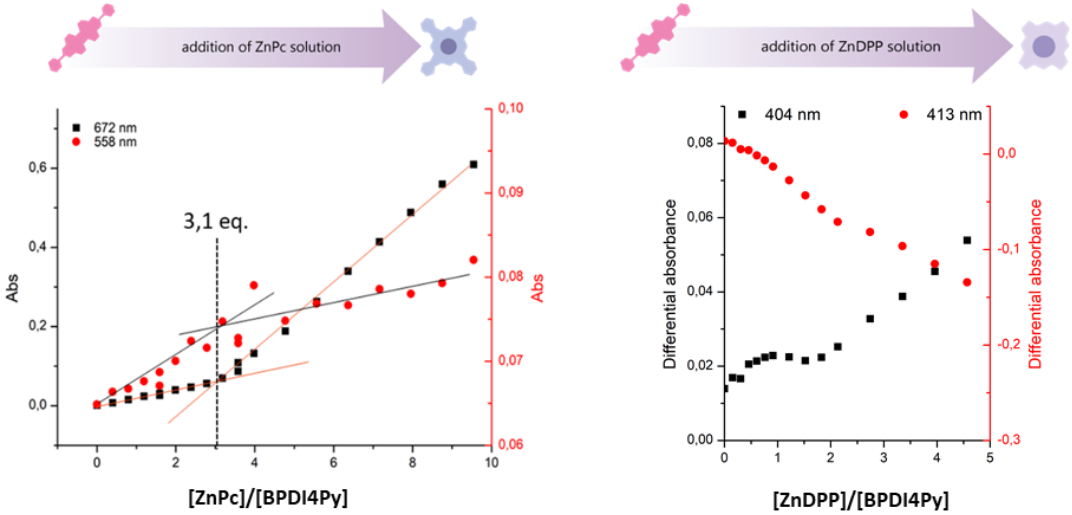


Figure S3. Plot of the maximum absorbance peaks of (left) ZnPc (672 nm, in black) and the BPDI4Py (558 nm, in red) against the ratio of ZnPc/BPDI4Py added in $CHCl_3$. The ZnPc solution used presents visible aggregation, preventing the association with the BPDI4Py from happening. It is only after reaching approximately 3 eq that a change is observed, which could be attributed to an interaction between the BPDI4Py and the ZnPc. (right) Plot of the evolution of the ZnDPP-BPDI4Py dyad peak (404 nm) when ZnDPP is added to a BPDI4Py solution. We can observe two different regimes after the addition of around 1 and 2 equivalents of BPDI4Py (413 nm).

ZnDPP subtracted spectra – titration of BPDI4Py with ZnDPP

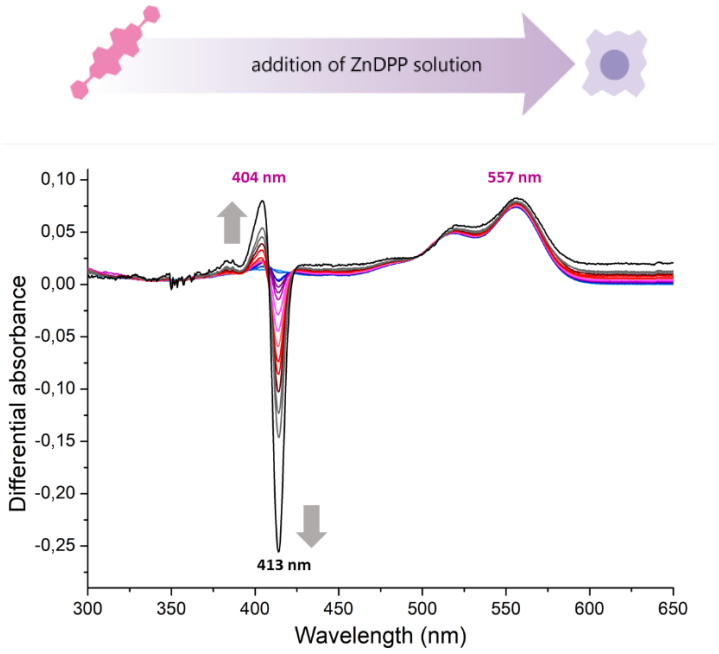


Figure S4. Absorbance spectra of the titration of BPDI4Py solution with ZnDPP. The absorbance spectra of the pure solution of ZnDPP has been subtracted from each acquisition considering the increasing volume as the titration takes place. The negative peak at 413 nm results from the subtraction of the pure ZnDPP spectra from the titration spectra. In theory, if no association is present, the subtraction of the ZnDPP signal would lead to no signal observed. Because we observe a negative signal, this means that the ZnDPP absorption is lower in the presence of BPDI4Py. Using this treatment, we were also able to perceive the appearance of a new signal at 404 nm, which we attribute to the ZnDPP-PDI4 complex.

Absorbance titration of ZnDPP with BPDI4Py

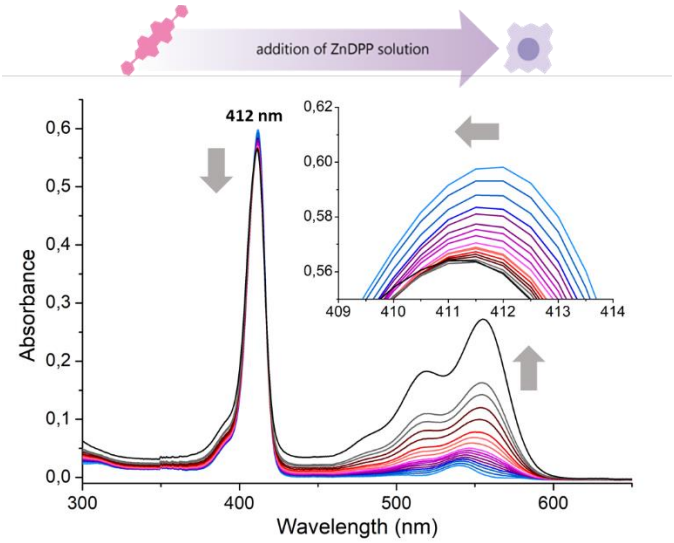


Figure S5. Absorbance titration of ZnDPP solution with increasing concentration of BPDI4Py in $CHCl_3$. As the titration progresses, we observe a decrease in the absorbtion maxima of the ZnDPP (413 nm), accompanied by a blue-shift (inset).

Absorbance titration of ZnPc and ZnDPP with BPDIC7

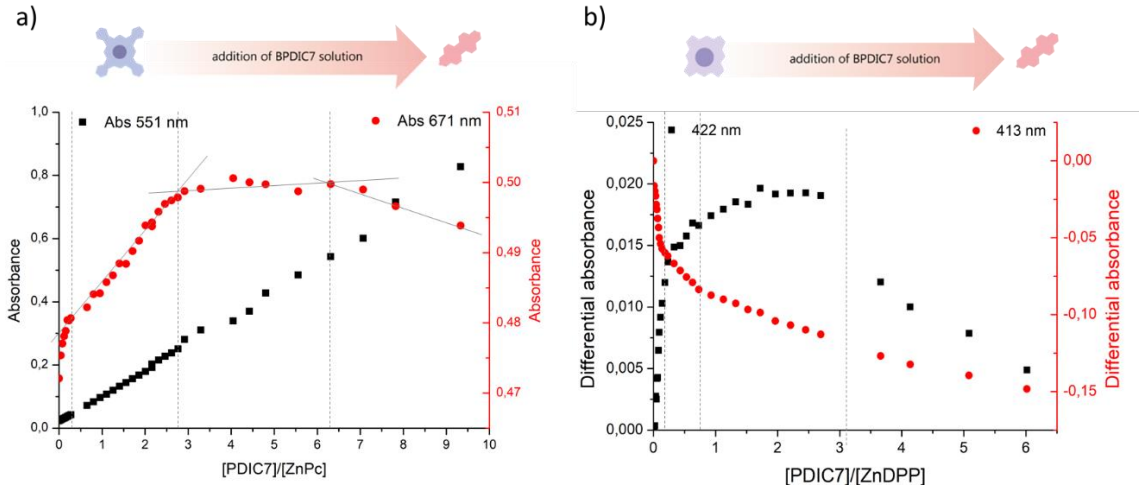


Figure S6. a) Titration of a ZnPc solution with BPDIC7. We observe three breaks in the intensity shift slope for the ZnPc's Q-band (671 nm) at 0.2, 2.7 and 6.3 equivalents of PDIC7 added. This result cannot be explained by a simple model of association, and all we can conclude is that multiple associations are present. We believe that a mixture of homo- and hetero-molecular aggregates, as well as supramolecular oligomers are the cause of this observations. This led us to the conclusion that we must also consider the π-π interactions between the BPDI4Py and ZnPc in the first titration experiment. **b)** Plot of the subtracted absorbance values from the titration of ZnDPP by BPDIC7. In this case, a red-shift of the Soret band of the ZnDPP was observed. The decay of absorption monitored at 404 and 413 nm doesn't match with any standard 1:1 or 1:2 association models. The growth of the 422 nm peak followed by a strong decay could only be explained by the formation of supramolecular oligomers. Thanks to this reference experiment with BPDIC7 we can say that the π-π interactions between different species can't be neglected either.

Fluorescence titration of ZnPc with BPDI4Py

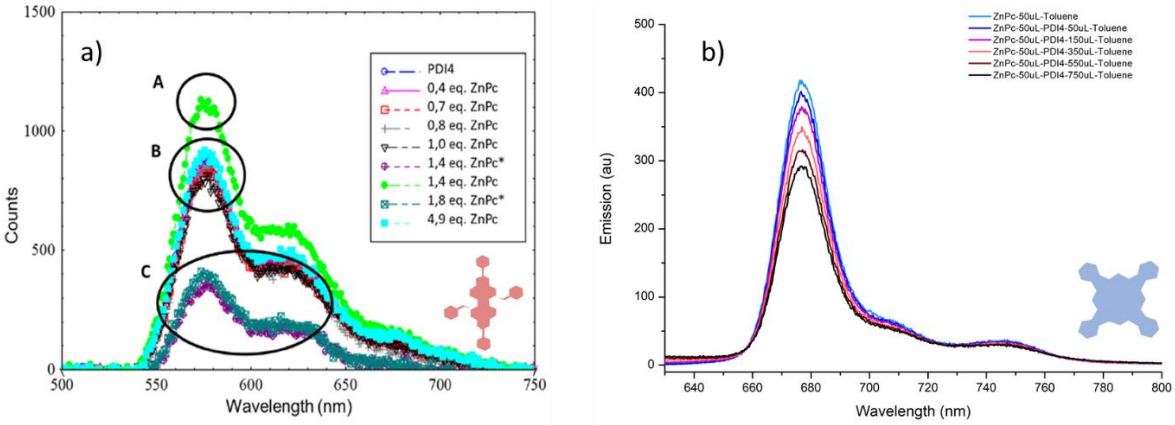


Figure S7. a) Emission spectra of BPDI4Py with increasing concentration of ZnPc in toluene. The solution was excited at 532 nm. Zone A shows a high-intensity signal which is supposed to correspond to 1.4 equivalents of ZnPc added. This result seemed somewhat abnormal and so a new solution was prepared. Zone B shows no quenching occurring on the PDI4's emission over increasing addition of ZnPc (0-1 equivalents), and no global trend of increasing or decreasing emission signals. In zone C, we see the emission using the new solution, whose intensity is lower than expected (x2 compared to the 1 eq.). We confirmed that this decrease in the signal is real by preparing a third solution this time with 1.8 equivalents of ZnPc. The emission observed is similar to the second solution prepared at 1.4 eq., so we deduced that after this ratio (1.4 eq.) BPDI4Py crystallises and precipitates.
b) Emission spectra of the ZnPc excited at 630 nm. The decay of the emission intensity observed was found to be directly proportional to the dilution factor.

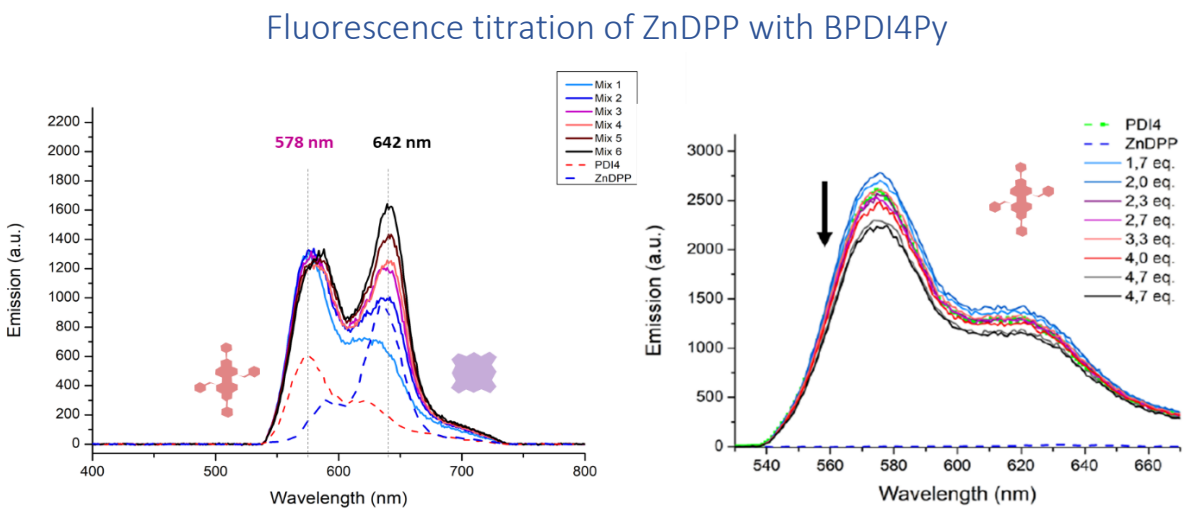


Figure S8. (left) Emission spectra of 0 to 1.2 equivalent addition of ZnDPP to BPDI4Py in toluene. Using a 415 nm excitation wavelength led to the emission of both the BPDI4P and ZnDPP which have overlapping absorption spectra. The increase of emission of ZnDPP at 642 nm was correlated with the increasing concentration in solution. The PDI4 peak at 578 nm was observed to be almost constant over the 1.2 equivalents of ZnDPP added. (right) Emission spectra of BPDI4Py with increasing amounts of ZnDPP added, and excited with a 520 nm wavelength. Here, only the emission of the BPDI4Py could be observed. From 0 to 1.2 equivalents of ZnDPP, we observed a decrease in intensity which was found to be directly correlated to the dilution factor. The volume increased by 15% over the addition and the emission collected decreased by the same amount. From this data, we found no evidence of association since neither the emission wavelength or the intensities of both ZnDPP and PDI4 are affected.

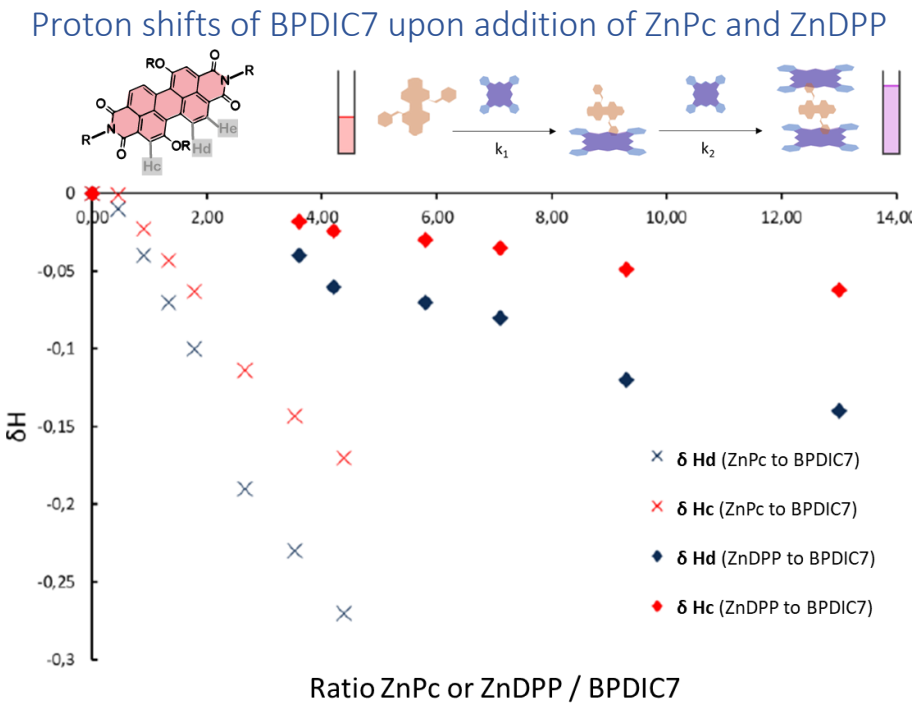


Figure S9. Plot of the **c**hemical shifts the Hc and Hd protons of the BPDIC7 with the increasing quantity of ZnPc (cross) and ZnDPP (lozenge). We observe a stronger shielding effect with the ZnPc addition compared to the ZnDPP. The shifts observed for ZnDPP behave in a near-linear fashion. After 4 equivalents of ZnDPP added we see almost no interaction between ZnDPP and BPDI4Py so we believe the π-stacking between the molecules is negligible compared to the zinc pyridyl coordination of ZnDPP-BPDI4Py. In the case of ZnPc and BPDIC7, the shift of 0.3 ppm after 4 equivalents of ZnPc added show a stronger interaction. Thus, we can affirm that the BPDIC7 interacts via π-π stacking with both ZnPc and the ZnDPP in a lesser extent. This interaction is somewhat weaker with PDIC7 compared to PDI4 because of the presence of the alkyl chains.

Determination of the association constant via NMR titration (*via* supramolecular.org)

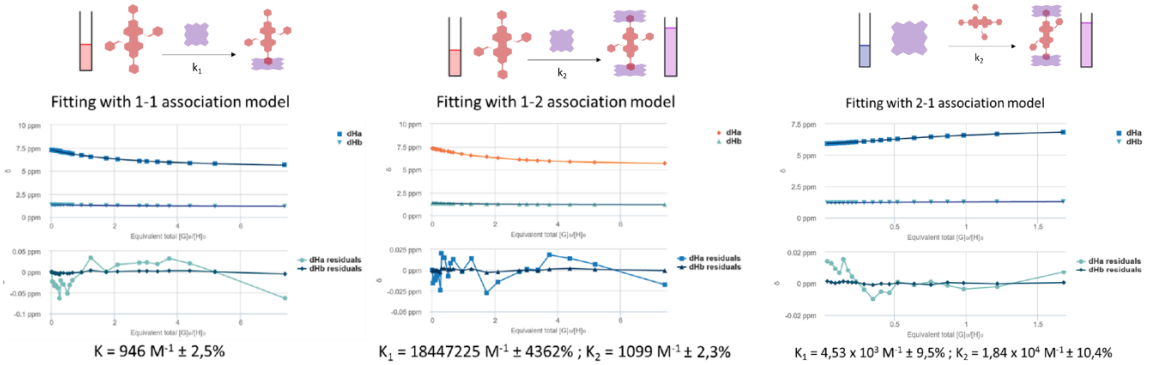


Figure S10. Nelder-Mead fitting of the NMR data ZnDPP-BPDI4Py. [G] is the ZnDPP guest and the BPDI4Py, the host [H]. On the right (top to bottom) is the fitting using a 1:1 association model, the residual errors plot and the association constant. In the middle, we have the fitting using a 1:2 association model, the residual errors plot and the association constants. Finally, on the far right, we present the 2:1 model fitting for the titration of the reverse addition, this time with the ZnDPP as the host [H], and the BPDI4Py the guest [G].

STM studies on HOPG

The tip-sample bias voltage and tunneling current set points were kept between - 1000 mV and -300 mV and between 11 pA and 15 pA, respectively.

C12-TSB network and with the ZnPc and ZnDPP pedestals

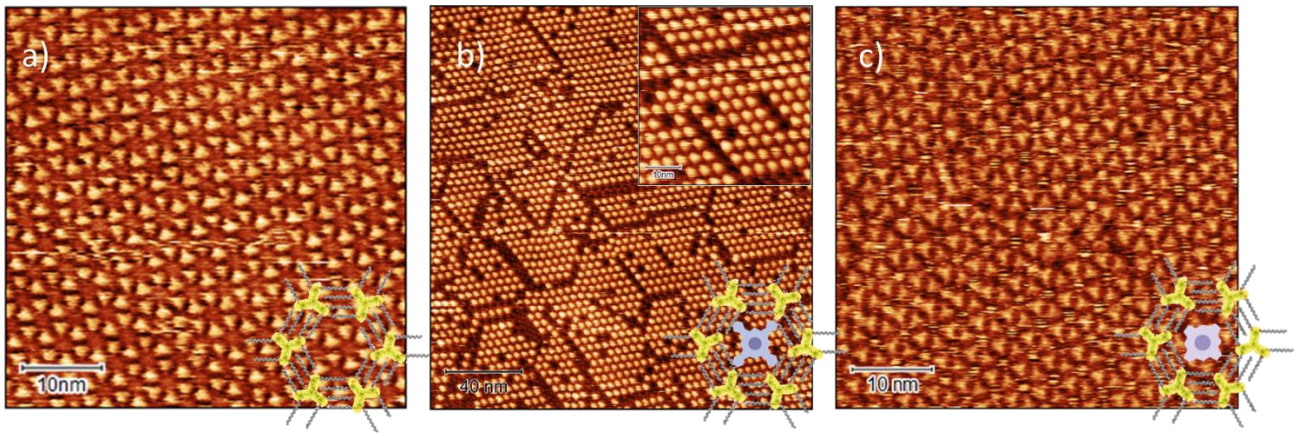
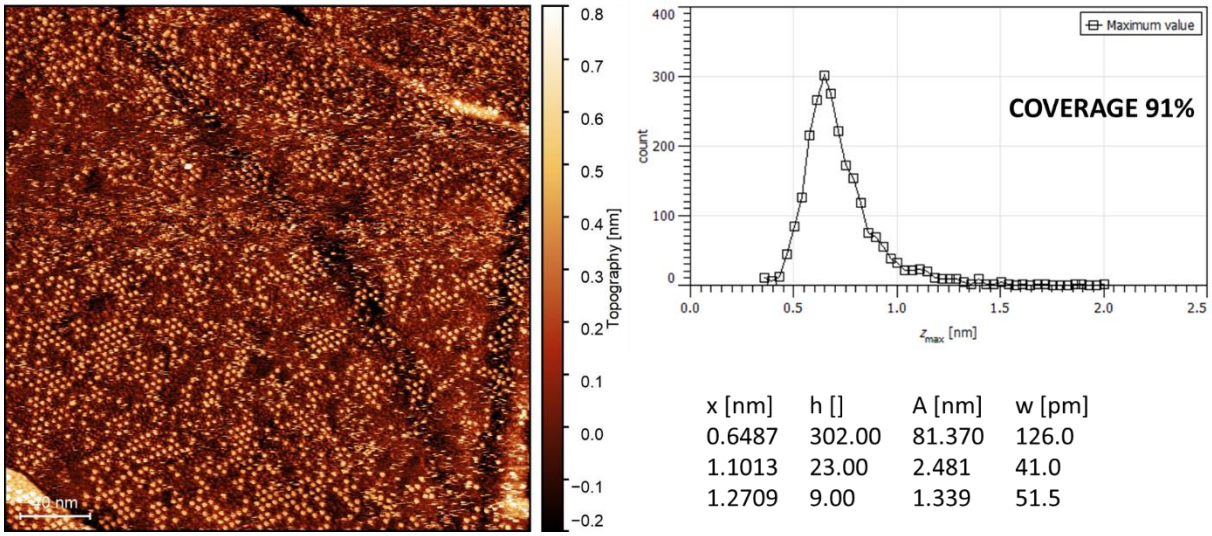


Figure S11. STM images of a) 50 nm^2 empty C12-TSB nanoporous network, b) a 190nm×190nm and (inset) 50nm^2 STM image of ZnPc filled pores on C12-TSB modified HOPG surface and c) 50nm×50nm STM image of ZnDPP filled pores on C10-TSB modified HOPG. Both (a) and (b) images were obtained at the liquid-solid interface using phenyloctane whilts (c) was obtained in air.

ZnPc-BPDI4Py coverage on HOPG



x [nm]	h []	A [nm]	w [pm]
0.6487	302.00	81.370	126.0
1.1013	23.00	2.481	41.0
1.2709	9.00	1.339	51.5

Figure S12. 300 nm^2 STM image of ZnPc-BPDI4 filled on C12-TSB modified HOPG surface at the liquid-solid interface using phenyloctane. resulting in a >90% coverage of ZnPc-BPDI4Py in the C12-TSB cavities.

Depot of BPDI4Py on C12-TSB network

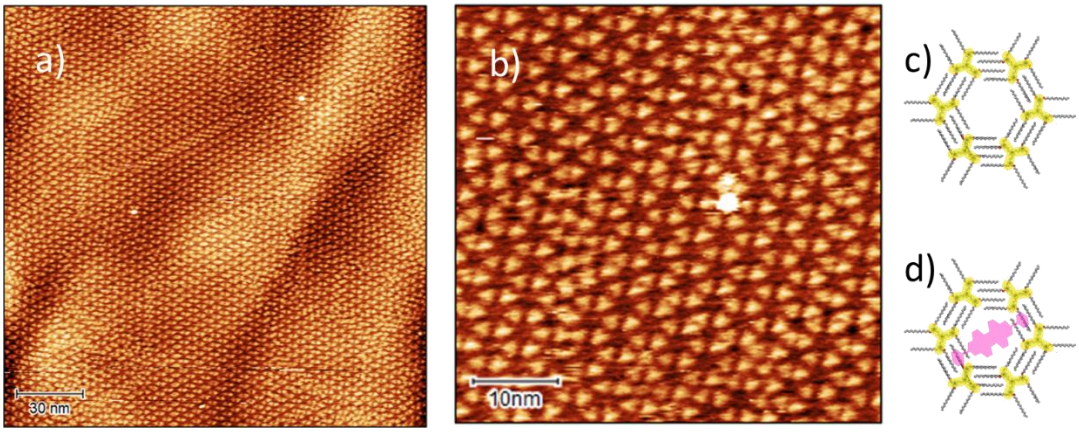


Figure S13. a) 100 nm^2 STM image of BPDI4 deposited on C12-TSB on HOPG. b) shows a zoomed-in image at 50x50 nm where one bright spot corresponding to the BPDI4PY in the TSB cavity ca be discerned (d). The rest of the image can be seen as the empty TSB cavities (c) All images were obtained at the liquid-solid interface using phenyloctane.

Topographic image of zoomed region (defects)

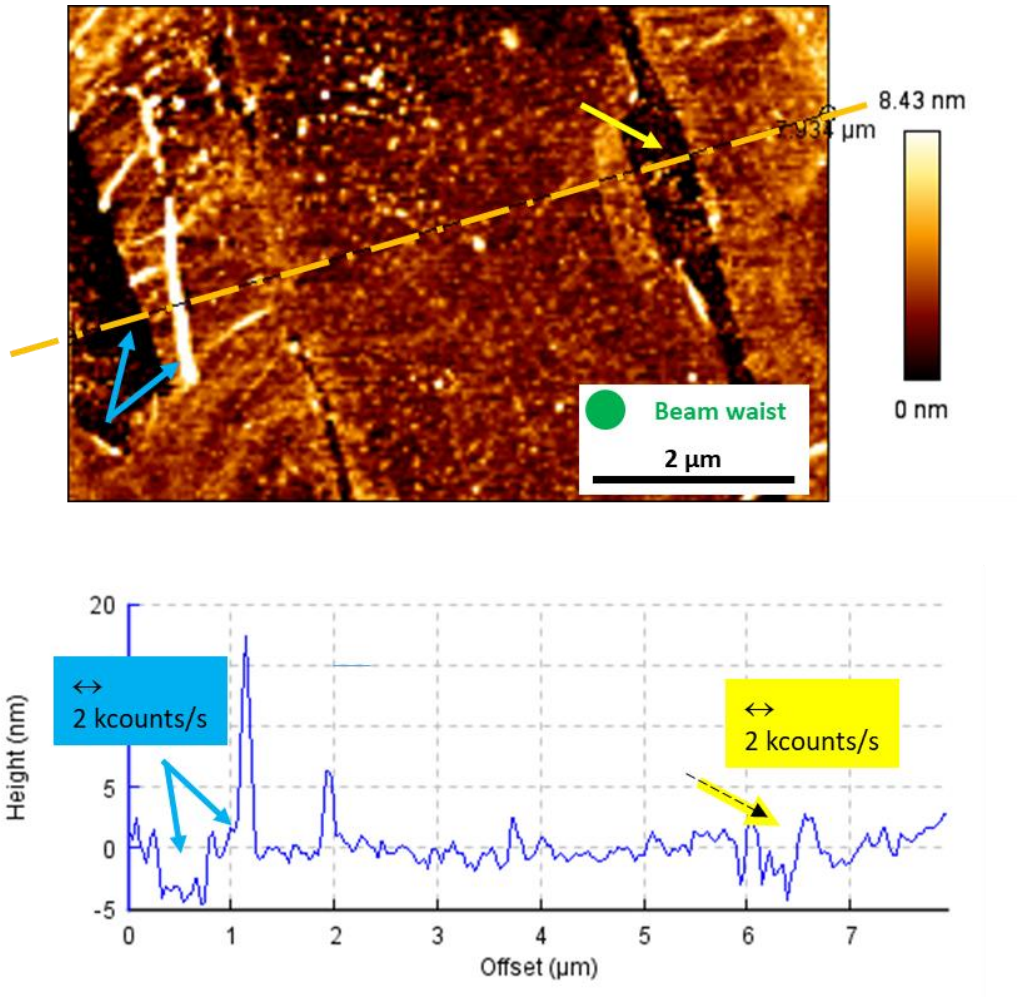


Figure S14. Detailed topographic image (tapping mode AFM) of the rectangle indicated in yellow in figure S14. A cross section is provided along the dotted orange line showing that quite comparable fluorescence emission can be obtained in areas of very different topographic nature (dip or peaks possibly coming from cracks or ripples in the graphene layer), the optical probe (materialized by a green disk) averaging the signal over quite large areas (~300 nm) compared to the changes in topography.