Supplementary information

Halogen bonding influences perylene-core twists in non-core substituted perylene tetraesters

Jonathan. P. Wojciechowski,[a,b] Adam. D. Martin,[a,b] Mohan. Bhadbhade,[a,c] James. E. A. Webb[a.b] and Pall. Thordarson*[a,b]

[a]School of Chemistry, The University of New South Wales, Sydney, 2052, NSW, Australia

[b]The Australian Centre for Nanomedicine and the ARC Centre of Excellence for Convergent Bio-Nano Science and Technology, The University of New South Wales, Sydney, 2052, NSW, Australia

[c]Mark Wainwright Analytical Centre, The University of New South Wales, Sydney, 2052, NSW, Australia

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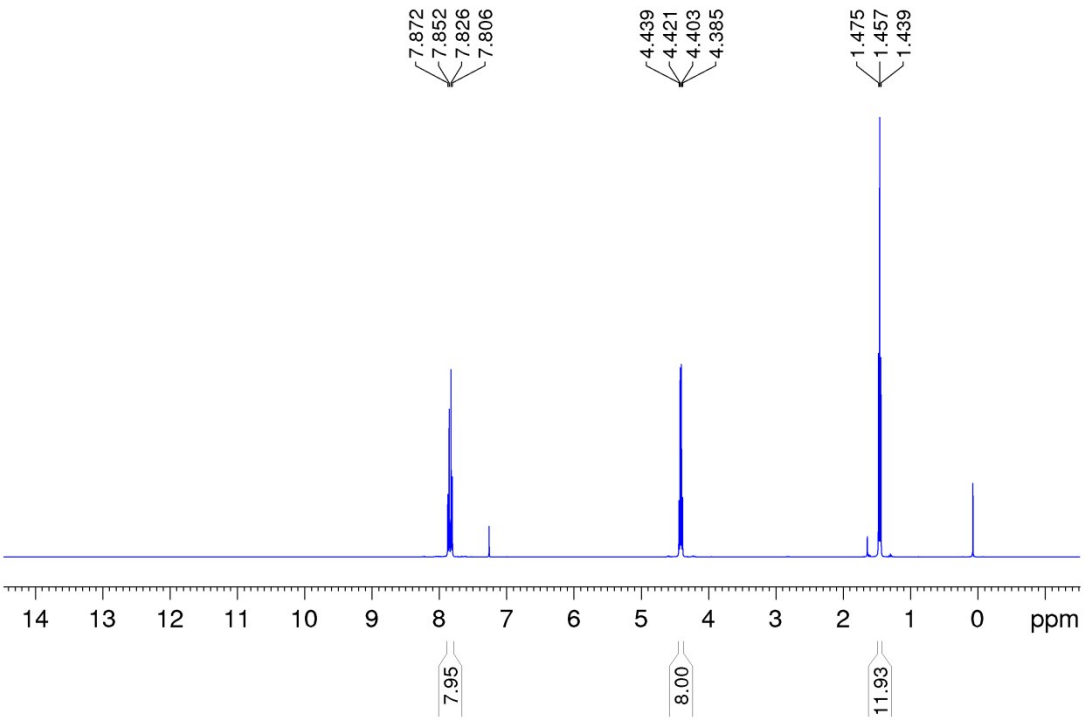
Methods

Synthesis of perylene-3,4,9,10-tetracarboxylic tetraethylester (PTE)

Perylene-3,4,9,10-tetracarboxylic tetraethylester was prepared according to a modified literature procedure.[1] A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (5.00 g, 12.7 mmol) and 1,8-diazabicycloundec-7-ene (20.0 mL, 134 mmol) in ethanol (6.00 mL, 103 mmol) was sonicated and stirred for 30 minutes to give a dark red solution. Iodoethane (8.20 mL, 103 mmol) was added to this mixture which was heated to reflux for 2 hours under nitrogen. The mixture was diluted with dichloromethane (100 mL) and the organic phase washed with water (x3), brine (x1), dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude mixture was purified *via* column chromatography using 99:1 dichloromethane/acetone as the eluent. Fractions were concentrated under reduced pressure to yield the title compound as a dark orange solid. (4.89 g, 71%).

^{1}H NMR (400 MHz, $CDCl_3$): 7.84 (1 H, dd, *J* 18.6, 8.0), 4.41 (1 H, q, *J* 7.1), 1.46 (2 H, t, *J* 7.2). ^{13}C NMR (101 MHz, $CDCl_3$): 168.62, 132.65, 130.36, 130.22, 128.70, 128.49, 121.27, 61.50, 14.34. This is good agreement with previous reports on PTE.[1]



^{1}H NMR for perylene-3,4,9,10-tetracarboxylic tetraethylester (PTE)

Crystallisation methods and crystal data

PTE

The solventless crystal structure was crystallised *via* two methods which both yielded the same structure. The first was slow evaporation from a solution of chloroform/hexane at 20 °C. The second, which has been previously reported, was slow evaporation from a solution of THF/ethanol at 20 °C.[2]

PTE·CH_2Cl_2

The dichloromethane included structure was crystallised *via* slow evaporation of a dichloromethane/hexane solution at 20 °C**.**

PTE·DCE

The 1,2-dichloroethane included structure was crystallised via slow vapour diffusion of hexane into a 1,2-dichloroethane solution at 4 °C.

PTE·$CHBr_3$

The bromoform included structure was crystallised via slow evaporation of a bromoform solution at 20 °C.

Hirshfeld surface analysis of the perylene crystal structures.

Hirshfeld surface analysis is a useful technique to identify intermolecular interactions in crystal structures.[3,4] Hirshfeld surface analysis was performed using CrystalExplorer 3.1.[5] Two parameters convey relevant information about contact distances between the molecules; these are the distances from the surface to the nearest atom interior (d_i) and exterior (d_e) to the surface. Distances which are less than the sum of the van der Waals radii and highlighted as red spots on the surface. These distances are binned into 0.01 Å intervals and plotted on a 2D surface to construct a fingerprint plot which maps out close intermolecular interactions. Generating a surface around the perylene tetraesters allows for a graphical visualization of key intermolecular interactions between surrounding molecules.

Fluorescence spectroscopy studies

Spectroscopy grade: (where possible) tetrahydrofuran, dichloromethane, 1,2-dichloroethane and bromoform was obtained from Sigma Aldrich and used without further purification.

Fluorescence spectroscopy was performed on a Cary Eclipse Fluorescence Spectrometer. The concentration used in all solvents was $2x10^{-6}$ M.

Binding studies with bromoform:

Bromoform was used as received (Sigma). NMR titrations were conducted in on a Bruker Avance III 400 spectrometer operating at a frequency of 400.13 MHz with the probe temperature maintained at 298 K. NMR titrations were performed maintaining the concentration around 2.0 mM of the perylene host constant, by dissolving the bromoform guest in the same host solution, followed by addition of that guest dissolved in the host solution to the NMR sample of the host (+ any previously added guest in host solution or other additives), delivered accurately using 10, 25 or 100 µL Hamilton Microlitre syringes. After each addition, the samples were shaken thoroughly within the air-tight screw-cap NMR sample tubes and then allowed to equilibrate in the NMR probe for 1 min before the spectra were recorded.

Two different proton resonances were recorded (the 1,6,7 and 12 H-resonance and the 2,5,8 and 11 H-resonance), providing two sets of data from which the association constants can be determined by fitting to binding models using a custom written *python* program *BindFit* developed and deployed on the web[6] by A/Prof. Pall Thordarson and based on previously published binding programs.[7] The full set of scripts for BindFit is available at www.supramolecular.org[4] under the source code option (Help→Source code).

In the paper two different binding models are considered (see previous work for full details on the equations and terminology used here).[8]

1:1 equilibria. Here, we define the NMR resonance for the host as δ_H, the guest as δ_G and the host-guest complex as δ_{HG}. From this, we can also define the change in resonance for the host-guest complexation as $\delta_{\Delta HG} = \delta_{HG} - \delta_H$. If we then define δ_0 = NMR resonance of the host before the guest is added (before the start of titration) we can define the change in in resonance as $\Delta\delta = \delta - \delta_0$. We can now write the NMR version of our simple 1:1 equilibria according to equation (S9) which is derived from the generic quadratic equation used to calculate the concentration of host-guest complex [HG] as previously described.[7,8]

$$\Delta\delta = \frac{\delta_{\Delta HG}}{[H]_0}\left(\frac{1}{2}\left\{\left([G]_0 + [H]_0 + \frac{1}{K_a}\right) - \sqrt{\left([G]_0 + [H]_0 + \frac{1}{K_a}\right)^2 + 4[H]_0[G]_0}\right\}\right) \quad \text{Eq. (S1)}$$

Statistical 1:2 model. Here we make the assumption that the binding is non-cooperative ($K_1 = 4K_2$) and that the chemical shift changes are simply additive $\delta_{\Delta HG_2} = 2\delta_{\Delta HG}$.[7] This means in other words we make the assumption that the two binding site behave like two independent hosts. This yields equation (S2).[7]

$$\Delta\delta = \frac{\delta_{\Delta HG} K_1[G](1 + 2K_2[G])}{1 + K_1[G] + K_1K_2[G]^2} \quad \text{Eq. (S2)}$$

In this **statistical 1:2** model we have therefore made the assumptions that $K_1 = 4K_2$ and that $\delta_{\Delta HG_2} = 2\delta_{\Delta HG}$. It follows that the data could also be fitted to the simple **1:1** model according to Equation (S1) by simply multiply the total host concentration $[H]_0$ by a factor of 2. The resulting association constant K_a is then equal to the non-coopeartive microscopic binding constants, i.e. $K_a = K_{1m} = K_{2m}$, which means $K_1 = K_a/2$ and $K_2 = 2K_a$.

Results:

The raw input data, the calculated fit, statistical information and associated information can be accessed via the www.supramolecular.org[4] database through the below unique URL: (copy-paste into a web-browser)

i) Results for 1:1 equilibria:

http://app.supramolecular.org/bindfit/view/490904c7-68b6-45e7-b73f-13961872c1b1

ii) Results for statistical 1:2 equilibria (using the 1:1 model after multiplying host concentration by a factor of 2).

http://app.supramolecular.org/bindfit/view/736a3f5d-c635-48a6-9519-897f6137e25e

Figures

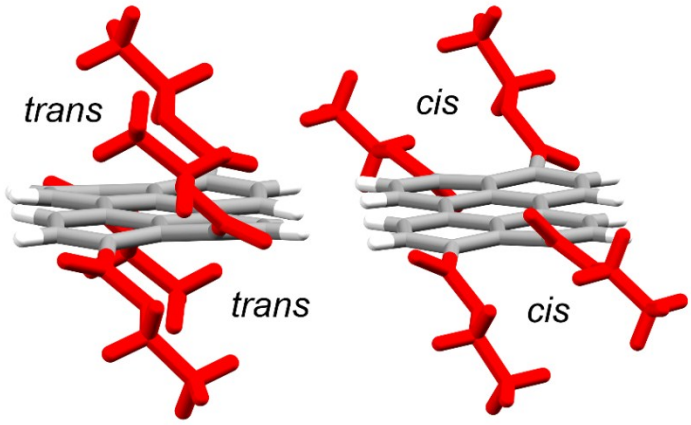


Fig. S1 Configuration of the ester groups on the perylene tetra esters observed in the crystal structures. The ester functional groups can lie trans/trans or cis/cis depending on the packing parameters. The trans/cis arrangement was not observed in the crystal structures used in this study.

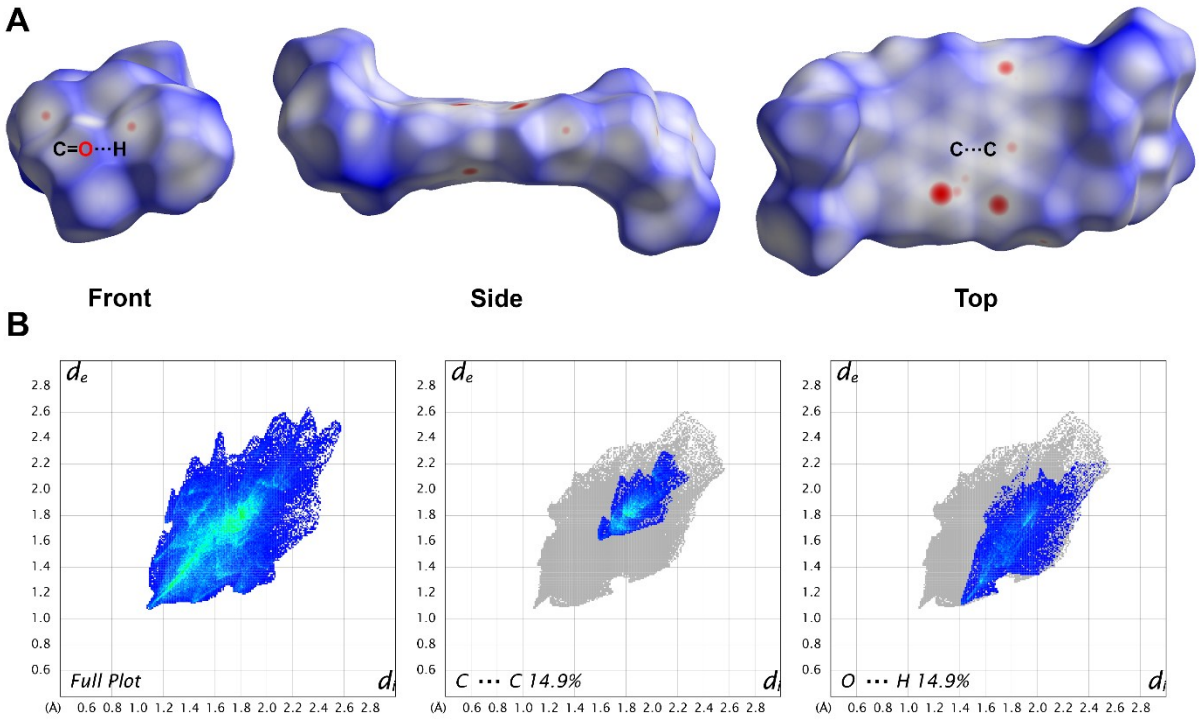


Fig. S2 Hirshfeld surface (A) and fingerprint plots (B) generated for PTE. The structure is largely dominated by C···C interactions and hydrogen bonding through the ester groups. This is shown as red points on the surface (A). The fingerprint plots show the distances over which these interactions occur and the percentage contribution to the total intermolecular interactions in the structure.

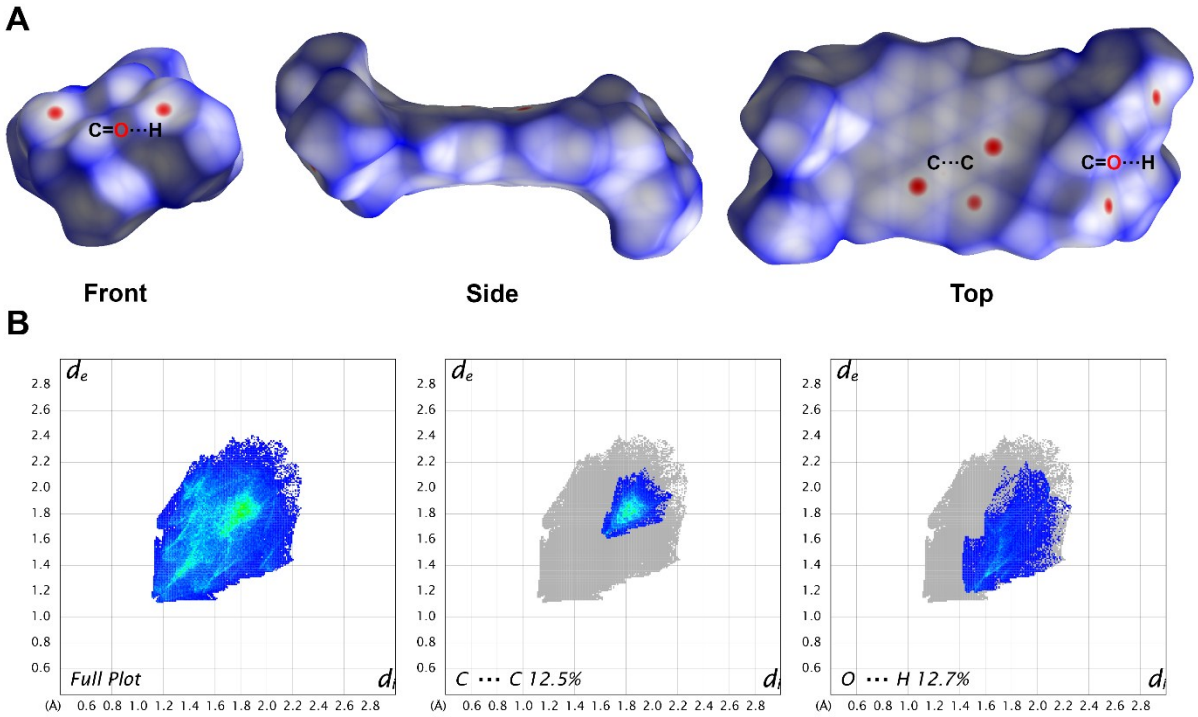


Fig. S3 Hirshfeld surface (A) and fingerprint plots (B) generated for PTE·DCE. The structure is largely dominated by C···C interactions and hydrogen bonding through the ester groups similar to PTE. This is shown as red points on the surface (A). The fingerprint plots show the distances over which these interactions occur and the percentage contribution to the total intermolecular interactions in the structure.

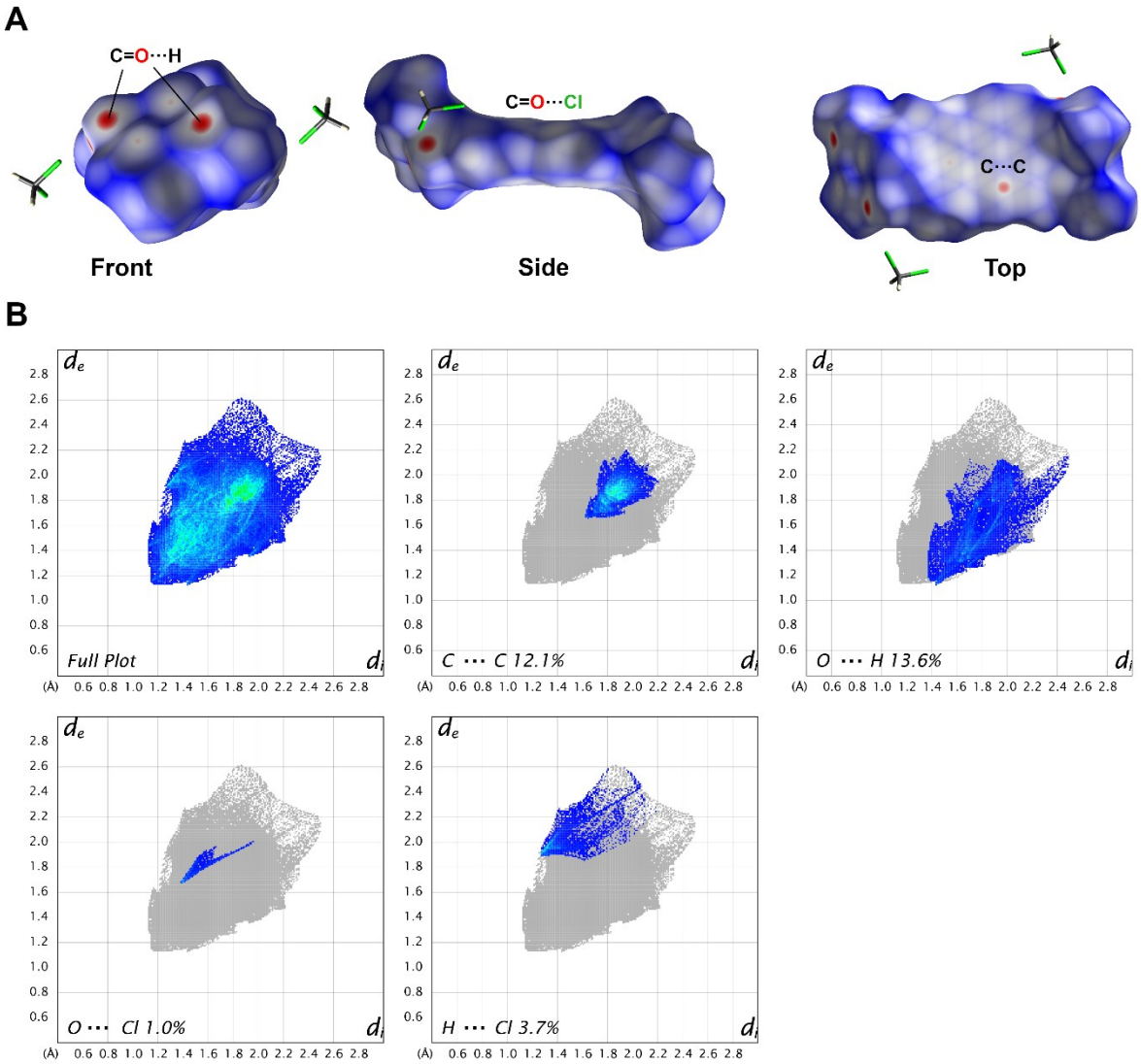


Fig. S4 Hirshfeld surface (A) and fingerprint plots (B) generated for PTE·CH_2Cl_2. The structure has decreased C···C interactions and increased hydrogen bonding through the ester groups compared to PTE. Halogen bond interactions (C=O···Cl) through the carbonyl group to dichloromethane are also highlighted.

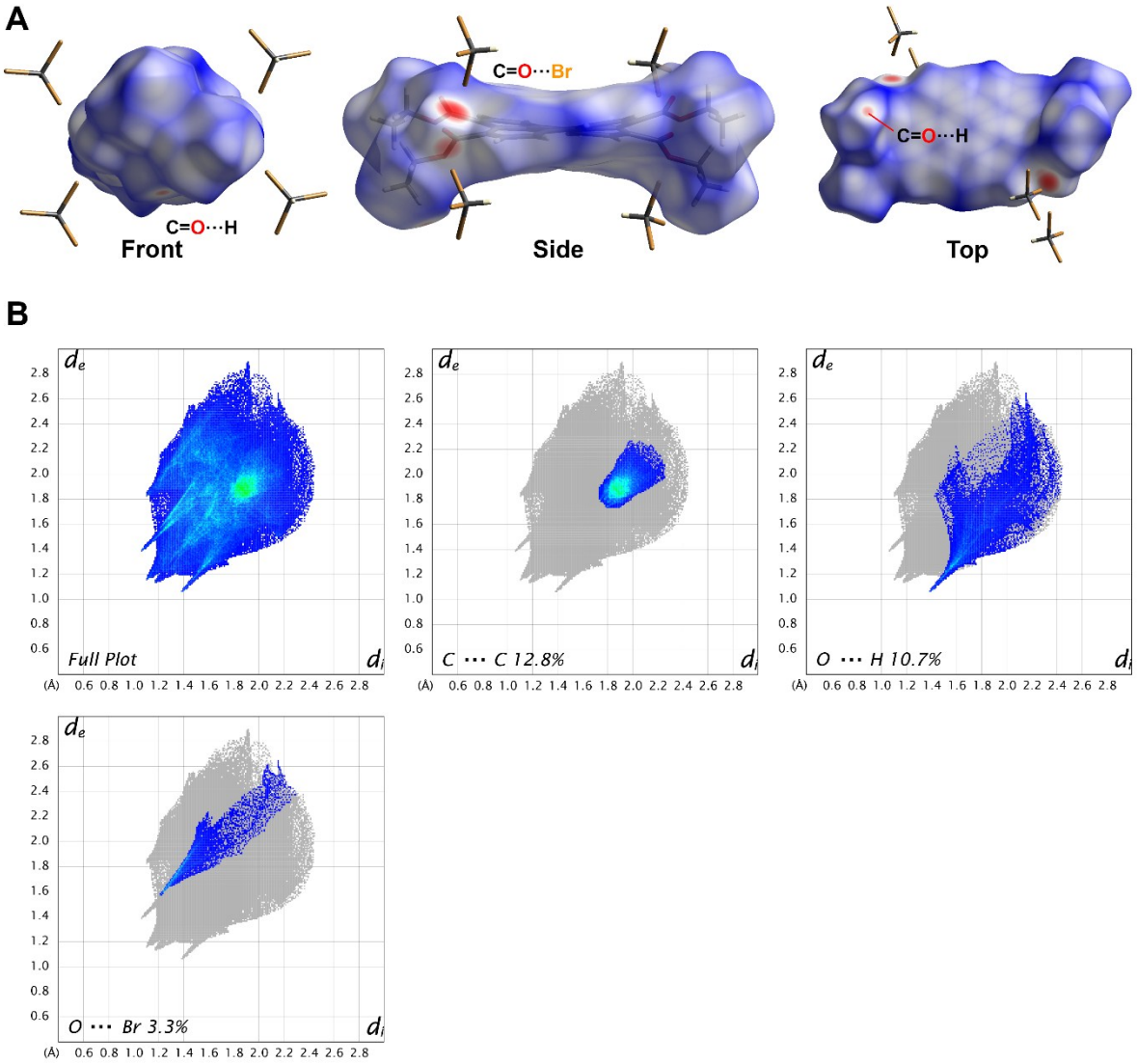


Fig. S5 Hirshfeld surface (A) and fingerprint plots (B) generated for PTE·$CHBr_3$. The structure has no observed C···C interactions and largely decreased hydrogen bonding through the ester groups compared to PTE. Halogen bond interactions (C=O···Br) through the carbonyl group to bromoform largely dominate the intermolecular interactions of the structure.

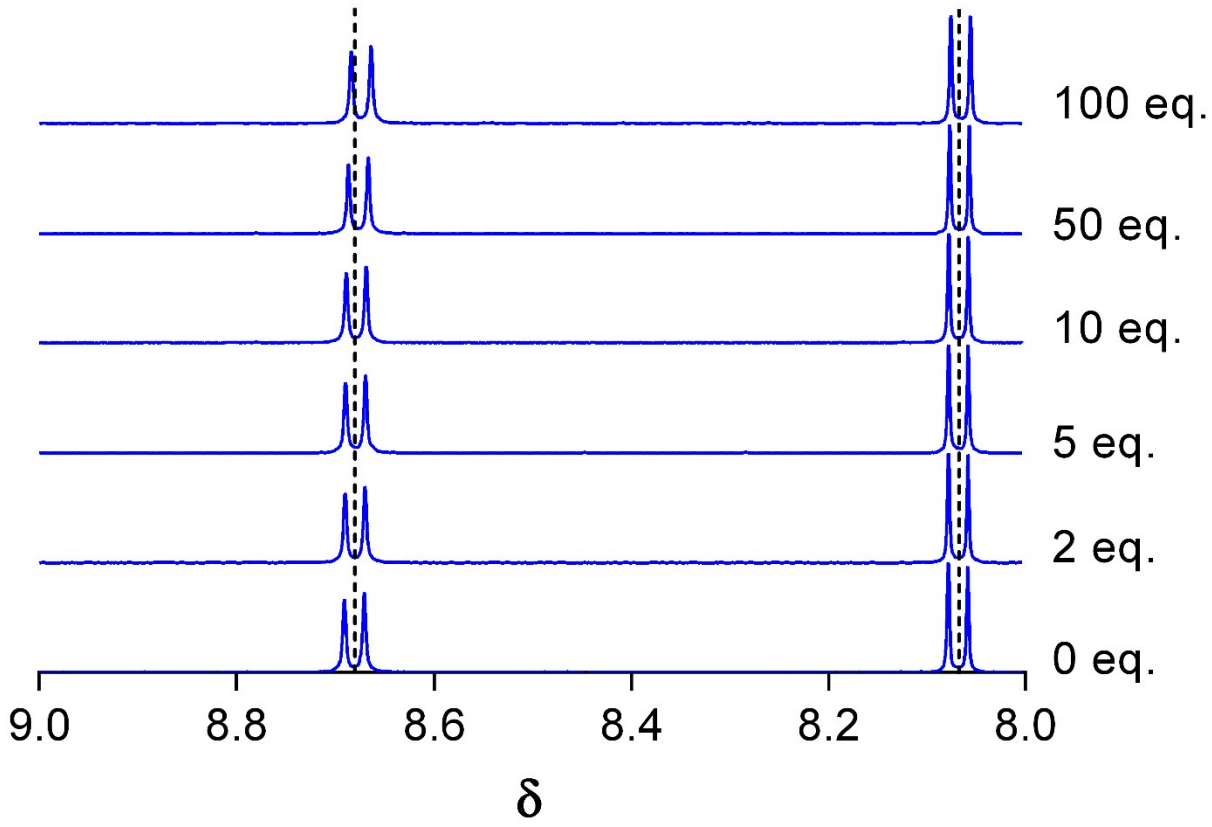


Fig. S6 ^{1}H NMR Titration of perylene-3,4,9,10-tetracarboxylic tetra ester with bromoform.

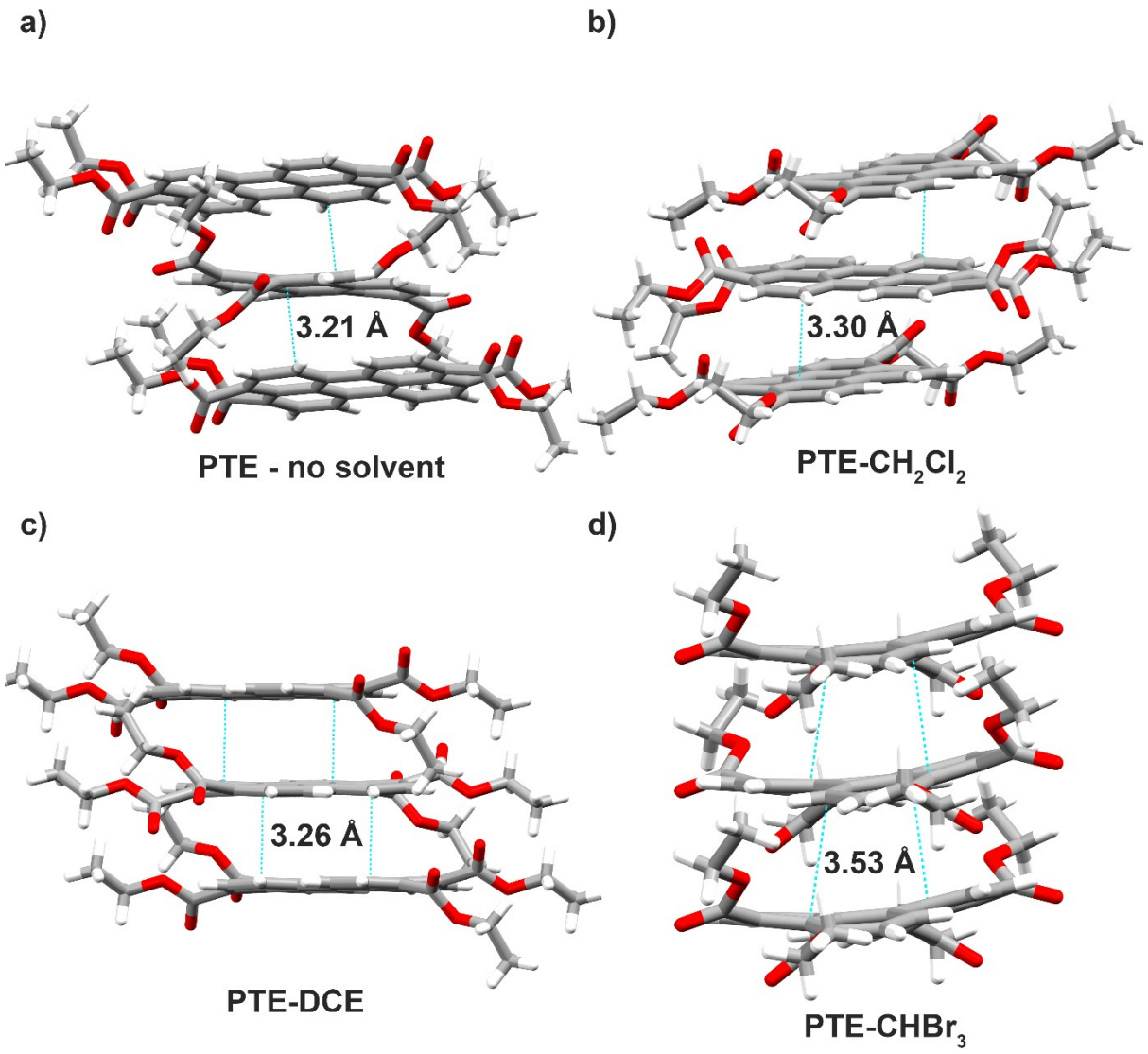


Fig. S7 Minimum π-π stacking distances found in the perylene tetraester solvates

References

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