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Dimeric Self-Association of an Isophthalamide Macrocycle in Solution and the Solid State

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Crystallisation Conditions

Polymorph I: An equimolar solution of macrocycle **1** and crystallisation agent **2** were dissolved in minimum acetonitrile. The vial was closed with a pierced lid and placed within a second sealed vial containing diisopropyl ether, allowing slow gaseous diffusion of the outer solvent into the sample vial. Plate-like colourless crystals grew over the course of a few days.

Polymorph II: This was obtained upon repetition of the procedure for Polymorph I, giving colourless block-like crystals.

Polymorph III: The procedure was the same as that reported for Polymorph I, but using **3** instead of **2**, yielding colourless block-like crystals coated in a brown oil, presumably consisting primarily of **3**.

Methanol solvate: A portion of macrocycle **1** was added to methanol, in which is it poorly soluble at room temperature. Heating of the mixture resulted in a colourless solution which produced needle-like colourless crystals upon slow cooling to room temperature.

Dichloromethane solvate: The slow diffusion procedure described for Polymorph I was used, with **4** acting as the crystallisation agent, and a 1:1 mixture of dichloromethane and acetone taking the place of the acetonitrile. Colourless plate-like crystals were obtained.

Iodopentafluorobenzene solvate: A 1:1 mixture of macrocycle **1** and tetrabutylammonium chloride was dissolved in minimum iodopentafluorobenzene. This required heating, although the solution was then stable at room temperature. The vial was closed with a pierced cap and placed in a second sealed vial containing diisopropyl ether. Gaseous diffusion of this solvent into the first vial gave colourless needle-like crystals.

Acetone solvate: The procedure was as for Polymorph I, using a 1:1:1 mixture of **1**, **5**, and tetrabutylammonium chloride in acetone, into which diisopropyl ether was diffused. Colourless plate-like crystals were obtained.

Acetonitrile solvate: The procedure was as for Polymorph I, omitting the crystallisation agent, giving large colourless block-like crystals, which were repeatedly the same structure.

X-Ray Data Collection and Refinement

Single crystal X-ray diffraction data were collected either using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer, or (as specified in Table 1) using silicon double crystal monochromated synchrotron radiation (λ = 0.68890 Å) at Diamond Light Source beamline I19 on a custom built Rigaku diffractometer. Both diffractometers were equipped with a Cryostream N_2 open-flow cooling device,[1] and the data were collected at 150(2) K.

If using the Nonius machine, series of ω-scans were performed in such a way as to collect every independent reflection to a maximum resolution of 0.77 Å, aiming for 99.5 % completeness. Cell parameters and intensity data (including inter-frame scaling) were processed using the DENZO-SMN package.[2]

When using synchrotron radiation, ω-scans were performed such that a half-sphere of data was collected to a maximum resolution of 0.77 Å. Cell refinement, data reduction, and scaling were performed using the CrystalClear package.[3]

The structures were solved by direct methods using the SIR92 software[4] or by charge flipping using Superflip.[5] The structures were refined using full-matrix least-squares on F^2 within the CRYSTALS suite.[6] All non-hydrogen atoms were refined with anisotropic displacement parameters. Disordered portions were modelled using refined partial occupancies. Geometric and vibrational restraints were applied where appropriate to ensure physically reasonable models. The H atoms were usually located in the difference map, but those attached to carbon atoms were repositioned geometrically. Protic H atoms which could not be located in the difference map were positioned to satisfy hydrogen bonding requirements. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularise their geometry (C-H in the range 0.93-0.98 Å, N-H in the range 0.86-0.89 Å, and O-H = 0.82 Å and isotropic displacement factors in the range 1.2-1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints. After the construction of a stable, physically reasonable, and complete model, the weights were optimised,[7, 8] anomalous reflections were omitted, and absent high-angle data (in the case of poorly diffracting samples) was pruned using the Wilson plot.

IUCr CheckCIF/PLATON[9] was used to validate the structures, and warnings were dealt with as appropriate or justified using validation reply forms.

Full crystallographic data can be found in the cifs.

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Hirschfeld Fingerprint Plots

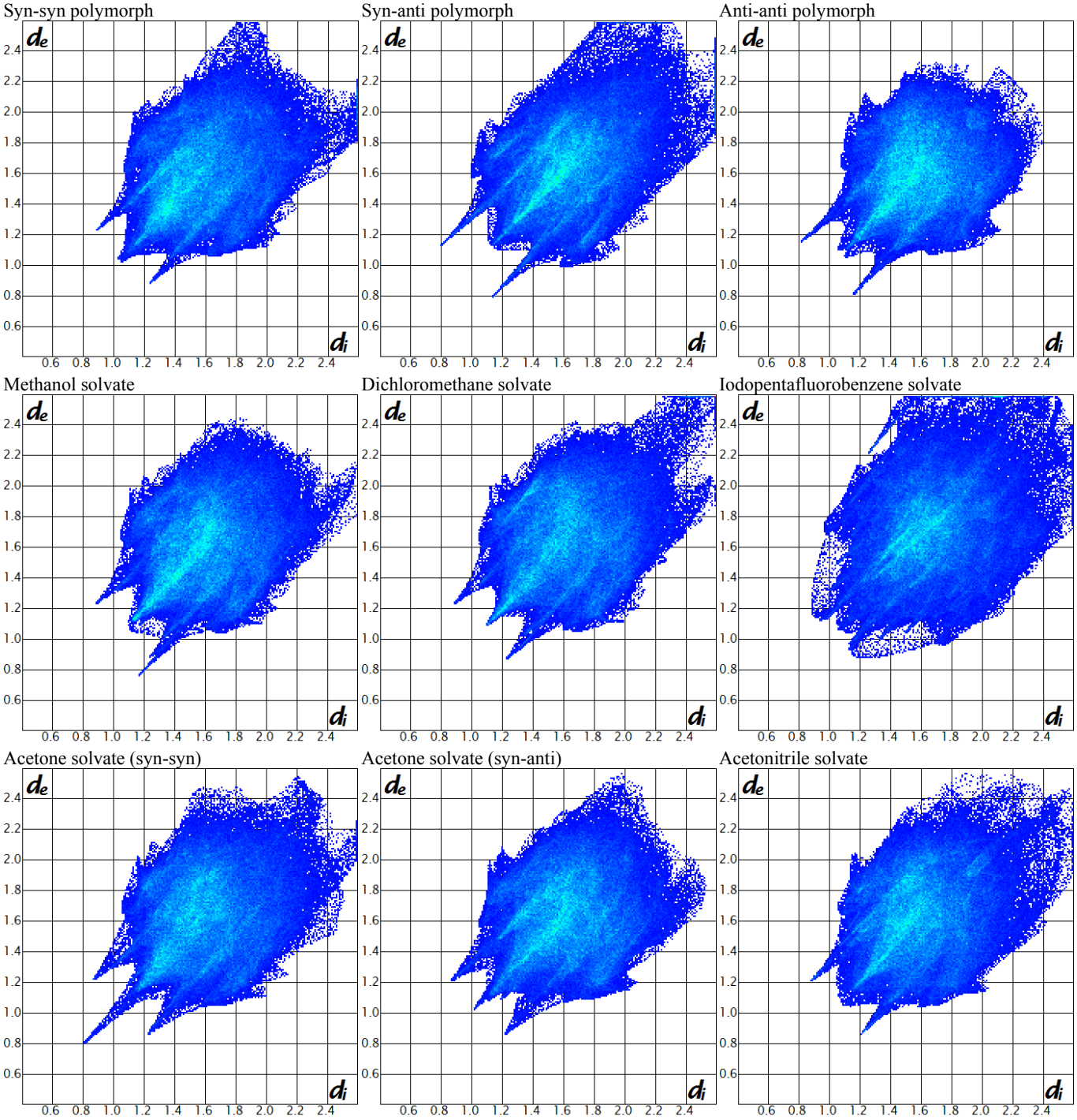

Figure S1 – Hirschfeld fingerprint plots for the crystal structures presented in this paper. The Hirschfeld surface fingerprint plots all display characteristic 'wing-tips' for short H – O contacts. In the iodopentafluorobenzene and acetone syn-syn cases these are obscured somewhat by disorder in the crystal structure.

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Solution NMR Studies

NMR data were collected on a Bruker AVII 500 MHz spectrometer operating with an inverse TXI probe. Diffusion experiments employed the bipolar LED stimulated echo sequence[10] with diffusion times Δ of 100 ms, diffusion encoding gradient durations δ of 4 ms (applied as half-sine shaped gradient profiles) and longitudinal eddy current delays (LED) of 5 ms. Total gradient strengths ranged from 0.7 to 22.1 G cm^{-1} applied as a linear ramp in 16 increments. Diffusion coefficients were obtained by fitting intensity decays using the Bruker routines in TOPSPIN 2.1 to: $I = I_0 \exp(-D\gamma^2\delta^2 g^2(\Delta-\delta/3))$ where I and I_0 represent signal intensities in the presence and absence of gradient pulses respectively, D is the required diffusion coefficient, γ is the ^{1}H magnetogyric ratio and g is the applied gradient strength (when corrected for sine-shaped gradient pulses). Diffusion experiments were performed at 298K in triplicate for each sample and diffusion coefficients were recorded as averaged values across all compound peaks within each spectrum. The reported coefficients are the mean values across the three experiments and errors reported as standard deviations between these.

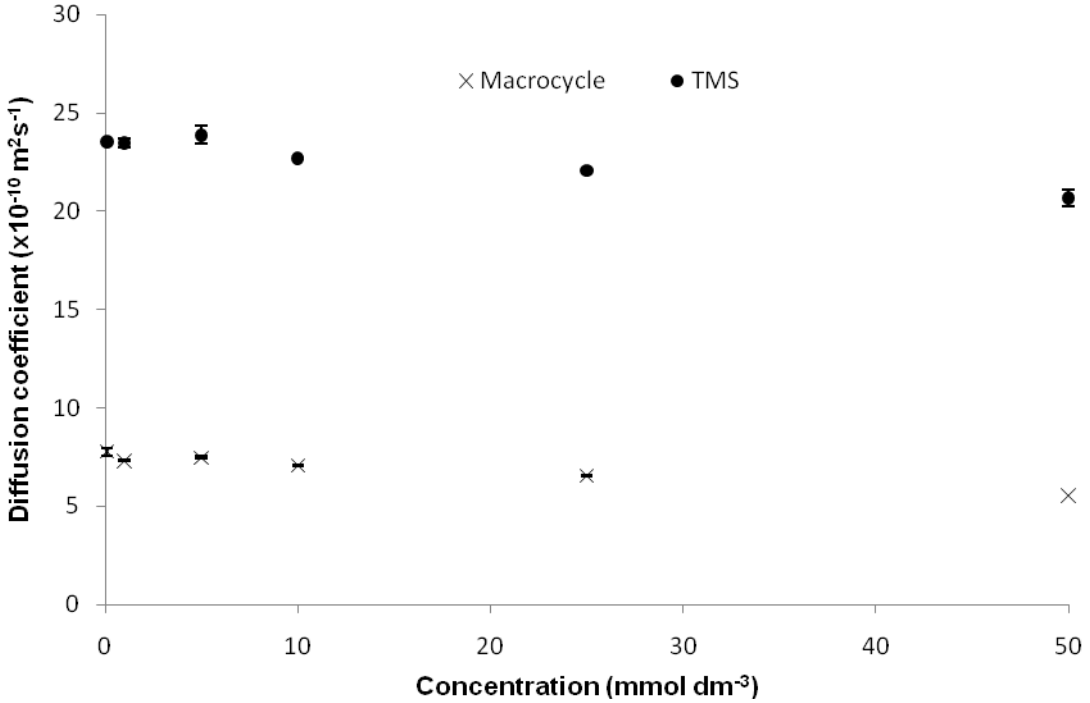

Figure S2 – Diffusion coefficients of macrocyle **1** and internal reference tetramethylsilane (TMS) as a function of solution concentration. Errors bars show standard deviations across triplicate data acquisitions and are within the symbol dimensions in some cases.

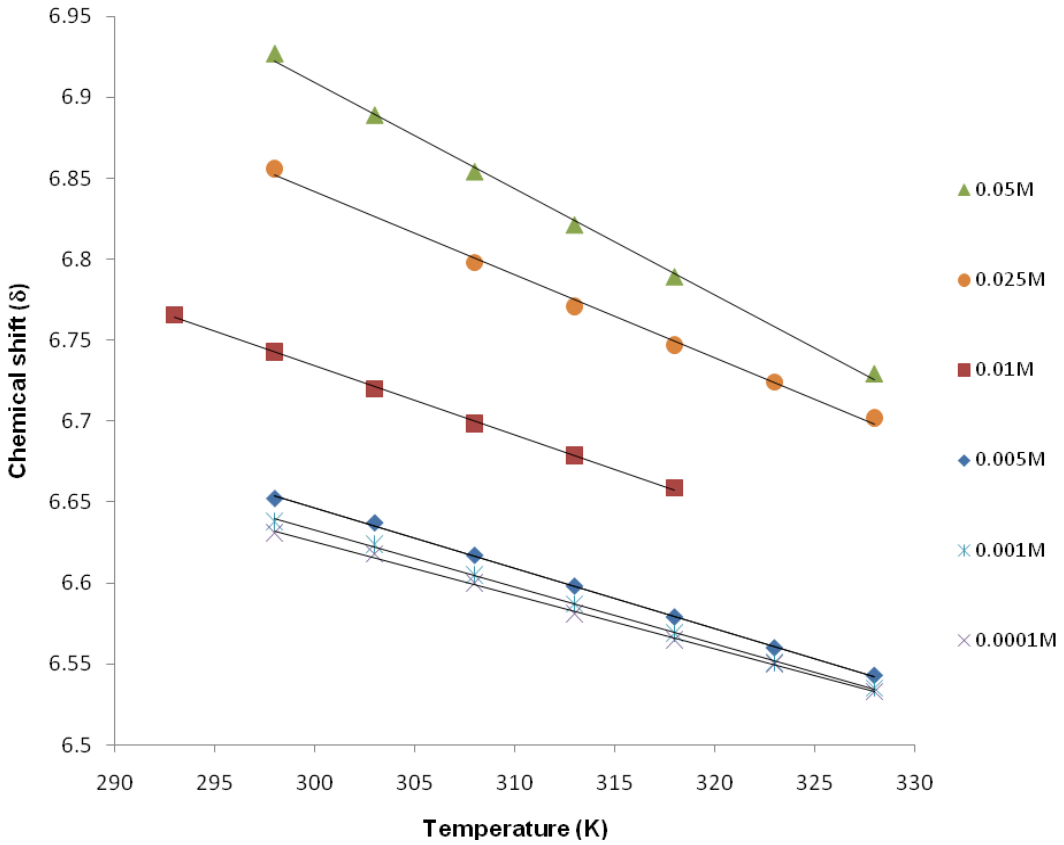

Figure S3 – Amide proton chemical shift temperature dependences across a series of solution concentrations. Temperature coefficents $\Delta\delta_T$ are derived from the slopes of linear regression fits and are presented in Fig 6.

References

1. J. Cosier and A. M. Glazer, *J. Appl. Cryst*, 1986, **19**, 105-107.
2. Z. Otwinowski and W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, Academic Press, 1997.
3. , Rigaku, 2009.
4. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst*, 1994, **27**, 435.
5. L. Palatinus and G. Chapuis, *J. Appl. Cryst*, 1997, **40**, 786-790.
6. P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst*, 2003, **36**, 1487.
7. J. R. Carruthers and D. J. Watkin, *Acta Cryst.*, 1979, **A35**, 698-699.
8. D. J. Watkin, *Acta Cryst.*, 1994, **A50**, 411-437.
9. J. C. C. Chen and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 2000, 839-840.
10. D. Wu, A. Chen and C. S. Johnson, *J. Magn. Reson. (A)*, 1995, **115**, 260-264.