ChemComm

COMMUNICATION

View Article Online
View Journal

Cite this: DOI: 10.1039/c5cc00507h

Received 19th January 2015,
Accepted 8th April 2015

DOI: 10.1039/c5cc00507h

www.rsc.org/chemcomm

Aromatic donor–acceptor interactions in non-polar environments†

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We have evaluated the strength of aromatic donor–acceptor interactions between dialkyl naphthalenediimide and dialkoxynaphthalene in non-polar environments. ^{1}H NMR, UV-vis spectroscopy and isothermal titration calorimetry were used to characterise this interaction. We concluded that the strength of donor–acceptor interactions in heptane is sufficient to drive supramolecular assemblies in this and other aliphatic solvents.

Donor–acceptor (D–A) aromatic interactions[1–4] have been shown to be a very useful tool in the field of supramolecular chemistry from self-healable polymers[5,6] to catenanes,[7] rotaxanes,[8–10] molecular assembly and binding,[11] charge separation and transport[12,13] dye sensitised solar cells and organic photovoltaic devices[14] or scavengers.[15] While they have been employed in many different research avenues, in the majority of cases polar solvent systems are used throughout. The use of such interaction in non-polar solvent systems in particular that of various donors with 1,3,5-trinitrobenzene has been previously reported by optical absorption or dispersed phase NMR methods.[16] We report herein our findings from a comprehensive study of the aromatic D–A interactions in heptane between two archetypal D–A partners: dialkoxynaphthalene (DN, donor) and dialkyl naphthalenediimide (NDI, acceptor). We use ^{1}H NMR, UV-vis and isothermal titration calorimetry to evaluate the strength of interaction between these molecules.

Although there is debate on the exact mechanism of the D–A aromatic interaction it is generally considered an electrostatically favourable face-centered stacking interaction between an electron rich aromatic molecule and an electron deficient aromatic counterpart.[1,2,17] Early studies of aromatic interactions have shown that there is a significant solvent dependence in all the systems studied.[18] Diederich and Smithrud's 1990 work[19] on the interaction of a pyrene guest with a cyclophane host in a large range of solvents from water to carbon disulphide, showed a linear free energy relationship between the free energy of binding and the polarity of the solvent. Cubberley and Iverson in 2001 studied[20] the solvent effect on the interaction between napthalenediimide and dialkoxynaphthalenes in a variety of solvents ranging from water (most polar) to chloroform (least polar). This also showed a quasi linear relationship between the polarity and free energy of formation (Fig. 1).

Both articles report a lower binding affinity between the D–A partners in non-polar solvents. However in both studies no aliphatic solvents were used.

More recently, Würthner and Chen investigated[21] the self-aggregation of perylenediimides (PDI) in a range of solvents from water to *n*-hexane (PDI had different side chains from one class of solvents to another in order to achieve desired solubility). In comparison to previous studies a linear relationship between the polarity and free energy of formation was not observed. It was shown that there was a decrease in the free energy of association with decreasing solvent polarity up until a minimum was reached in THF and toluene, followed by an increase in the free energy

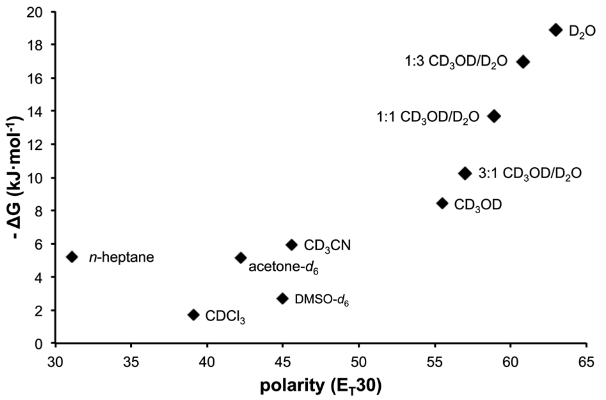

Fig. 1 Plot of $-\Delta G^\circ$ *vs.* the solvent polarity (E_T 30 scale) for NDI–DN interaction. The data for *n*-heptane is from this study while the rest was taken from ref. 20.

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† Electronic supplementary information (ESI) available: ^{1}H ^{13}C NMR HRMS data, NMR titrations and dilutions, UV-vis titrations, VT NMR, ITC. See DOI: 10.1039/c5cc00507h

of binding as the polarity decreased to hexane. It was also found that polarisable solvents such as $CHCl_3$, CH_2Cl_2 and DMSO were very efficient at solvating the PDIs, thus leading to low association constants, due to high dispersion forces. This trend was also observed in a study of reverse micelles by Silber *et al.*[16h] in which the binding constant between tetracyanoethane and naphthalene was four times higher in hexane than in chloroform (we observed qualitatively a similar behaviour, see ESI†).

We chose to study the interaction between the NDI and DN cores in order to compare their interaction in heptane with Iverson's seminal work[20] in more polar media, and because of their use in the assembling of catenanes and knots in polar solvents.[7,8] The NDI and DN cores used for this work were functionalised with 2-octyldodecyl alkyl chains to provide solubility in heptane. (NDI derivatives bearing ethylbutyl, ethylhexyl, 2-nonyl, dodecyl were also synthesised but were not soluble in heptane at >1 mM concentration range). We used the same solubilising side chain on both moieties in order to eliminate the influence of side chain interactions when comparing homo- with hetero-aggregates (DN **4** was synthesised in order to test if the side chains influence the assembly). The synthesis of DN derivatives **2** and **3** starts from commercially available 2-octyldodecan-1-ol which is converted in the corresponding bromide in 89% yield (Fig. 2).[22] The bromide is then converted into to the amine in a two step process using phthalimide and hydrazine, in a 81% overall yield.[23] The 1-amino-2-octyldodecane is reacted with 1,4,8,9-naphthalenetetracarboxylic anhydride (NDA) under standard[24] microwave assisted conditions to give the desired NDI in 94% yield. The synthesis of the DN counterparts used the 1-bromo-2-octyldodecane as starting material and 1,5- or 2,6-dihydroxynaphthalene. The reaction is conducted with excess bromide to prevent monoalkylation. While the reaction proceeds with good conversion, the dialkoxynaphthalene cannot be separated from the excess alkylating agent. To overcome this problem, phthalimide was added to the reaction in order to react with the excess bromide. The alkylated phthalimide was separated from the DN using column chromatography to give the latter in 47–50% yield over two steps. This procedure not only that allowed us to produce pure DN but also yielded the alkylated phthalimide that was used for the synthesis of NDI as described above. In the case of the synthesis of **4**, the excess bromide could be removed under high vacuum.

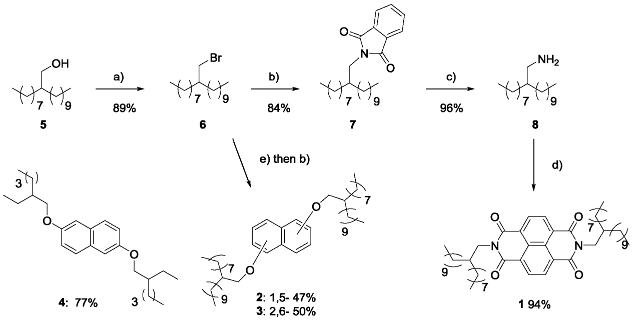

Fig. 2 The synthesis of NDI **1** and DN **2**, **3** and **4**; reaction conditions: (a) Br_2, PPh_3, THF, 3 h, 89% (b) potassium phthalimide, 90 °C, 18 h, 84% (c) H_4N_2, EtOH, reflux, overnight, 96% (d) NDA, DMF, 140 °C, 30 min, 94% (e) 1,5- or 2,6-dihydroxynaphthalene, K_2CO_3, MeCN, reflux, 24 h followed by (b), yield over two steps 47 or 50% for the 1,5- and 2,6-derivative, respectively.

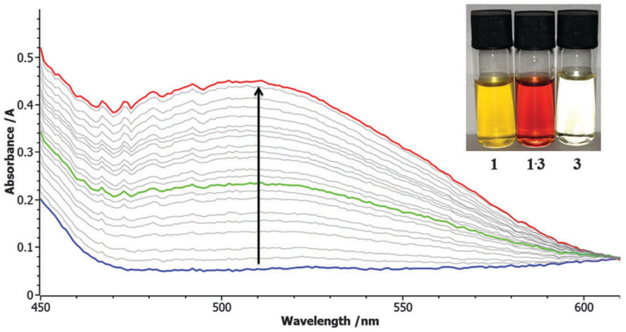

Fig. 3 Titration spectra carried out in heptane at 25 °C, initial concentration of **1** 25 mM with increasing amounts of **3**, 250 mM solution. (Blue = 0, green = 1 and red = 3 equiv. of **3**).

The first indication of interaction between the two cores came from mixing in a 1 : 1 ratio NDI : DN in heptane (25 mM concentration): a red colour is observed while the starting solutions are tan and light brown (Fig. 3). This behaviour is consistent with the formation of a charge transfer complex between the two cores.

In order to determine quantitatively how effective the association between the NDI and DN is in heptane, UV-vis, ^{1}H-NMR and ITC titrations have been performed on the individual components and on mixtures. When studying the association of any set of molecules *via* aromatic interactions, the self-association has to be taken in account. Dimerisation is the most obvious process that can occur, however supramolecular polymerisation[25,26] must also be considered.

In the case of NDI **1**, DN **2** and the **1·2** complex, variable temperature ^{1}H NMR experiments were carried out in a heptane : octane-d_{18} : 1,1,2,2-tetrachloroethane 95.1 : 4.8 : 0.1 solvent mixture. The data was then fitted with an isodesmic polymerisation model,[25,27] which indicated that at room temperature the majority of material exists as a monomer in the case of **1** (NDI 5.5 mM) ~85% with 13% dimer, 2% trimer or larger oligomers. In the case of **2**, isodesmic polymerisation model could not be fitted to the data, indicating that no self-aggregation was present. In the case of a **1·2** mixture (26.9 mM) 72% existed as the 1 : 1 complex, 22% as 2 : 2 species, 5% as 3 : 3 and 1% as higher oligomers. For simplicity,[28] we used the 1 : 1 complex as a 'monomer' in the isodesmic polymerisation model. These results confirmed that the dimerization process is dominant in this solvent and that the amount of larger oligomers is negligible, therefore all the titration data (^{1}H-NMR, UV-vis, ITC) was fit with either the dimerization or the 1 : 1 mathematical models were used (see ESI†).[29,30]

Dilution experiments were carried out *via* ^{1}H-NMR and ITC but not by UV-vis spectroscopy because of the high extinction coefficients of the aromatic cores which prevents accurate analysis of solutions with concentrations higher than 1 mM for NDI and 0.5 mM for 1,5- and 2,6-DN. The ^{1}H-NMR dilution experiments (25 to 3.6 mM) indicated that there is no significant association between the DN cores regardless of the substitution pattern, while for the NDI **1** a dimerisation constant of

Table 1 Self-association constants between the individual donor and acceptor molecular and the association constants between the donor and acceptor pairs[a]

Compound	K_a NMR[b] (M^{-1})	K_a UV[c] (M^{-1})	K_a ITC[c] (M^{-1})
1	3.4 ± 1	n/a	1.7
2	<1	n/a	<1
3	<1	n/a	<1
1 + **2**	8.3 ± 0.2	4.2 ± 0.3	11.5
1 + **3**	6.0 ± 0.3	4.9 ± 0.3	11.3
1 + **4**	6.9 ± 0.9	2.4 ± 0.3	6.1

[a] Single compound dilutions carried out at 25 °C. [b] The most downfield peak was monitored over a 25–3.6 mM conc. All the titrations used heptane : octane-d_{18} : 1,1,2,2-tetrachloroethane 95.2 : 4.8 : 0.1 as solvent. [c] Minimum value calculated by IC2ITC used see ESI.[31]

3.4 ± 1 M^{-1} was determined. These results were confirmed by ITC experiments (Table 1). The very weak dimerisation constants, which are two orders of magnitude lower than in water, indicate that the contribution of the solvophobic effect in heptane is very small when compared to water. (NDI–NDI dimerisation in water 200 M^{-1} *vs.* 3.4 M^{-1} in heptane; the dimerization constant in heptane is similar to those reported in CH_3CN or acetone).[20] Titration experiments were carried out *via* ^{1}H-NMR, ITC and UV-vis in order to determine the association constants between the NDI and DN. The ^{1}H-NMR experiments (25 mM initial NDI concentration) indicated the presence of a significant interaction between the donor (DN) and the acceptor (NDI) cores with association constants determined for **1** with **2**, **1** with **3** and **1** with **4** of 8.3 ± 0.2, 6.0 ± 0.3 M^{-1} and 6.9 ± 0.9 M^{-1}, respectively. The change in chemical shift on the NDI and DN aromatic protons is consistent with a face-centred stacking interaction (Fig. 4). These results also show that there is little or no geometrical preference or side chain influence for association as all DNs show similar K_a in their interaction with NDI **1**.

This was further confirmed by UV-vis spectroscopy, since the charge transfer band formed at 510 nm can be monitored at high concentrations (≤55.5 mM) allowing the determination of K_a of 4.2 ± 0.3 M^{-1}, 4.9 ± 0.3 M^{-1} and 2.4 ± 0.3 M^{-1} for **1**·**2**, **1**·**3** and **1**·**4** respectively (Fig. 3). A similar trend was observed by ITC, where association constants of 11.5, 11.3 and 6.1 M^{-1} were determined for **1**·**2**, **1**·**3** and **1**·**4** respectively. The reported values are the fit minimum value calculated by ICITC2 and due to working close to the detection limits of the instrument the errors associated with these values are large (Table 1 and ESI†).

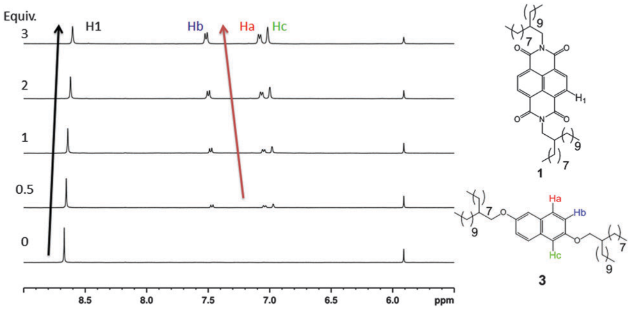

Fig. 4 ^{1}H NMR titration of **1** and **2** spectra at 0, 0.5, 1, 2, 3 equiv. of **3**. With increasing ratio of **3**, the aromatic proton signal of **1** moves upfield while the signal corresponding to H_b and to a lesser extent of H_a of **3** shifts downfield.

There are about two orders of magnitude difference between all K_a determined in water *vs.* heptane for the 1 : 1 NDI : DN mixtures (by ^{1}H NMR: 8.3 M^{-1} in heptane; 2000 M^{-1} in water[20]). This strengthens the argument (*vide supra*) that the solvophobic effects have a lower contribution in heptane when compared to water.[32] It is however noteworthy that the molecules show no association in chloroform regardless of the presence or absence of a complementary D–A partner.

We have shown that not only aromatic donor–acceptor interactions are possible in aliphatic solvents, but also that they lead to significant association between complementary aromatic cores. There is little or no geometrical preference for the interaction between NDI and 1,5- or 2,6-DN isomers, or side chain dependence. We believe that this works demonstrates that supramolecular architectures, similar to the numerous examples in aqueous media, could be constructed in non-polar aliphatic media.

We thank the EPSRC, BP, the EPSRC NMSF, the BMSS and the University of Bath for Financial Support. SIP thanks the Royal Society for a University Research Fellowship. We also thank Dr Nick Buurma for helpful discussions regarding the ITC experiments and IC2ITC software, and Mr Liam Emmett for helpful discussions regarding theoretical and experimental aspects of the project.

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