Segregated assemblies in bridged electron-rich and electron-poor π-conjugated moieties†

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We report a general strategy for the spontaneous segregation of electron-rich and electron-poor π-conjugated moieties using mutually phobic aliphatic fluorocarbon–hydrocarbon interactions.

Electron-rich π-conjugated molecules favorably interact with electron-poor π-conjugated molecules.[1] This interaction has been used to construct interesting supramolecular structures and sensors.[2] However, in organic-based devices such as photovoltaic cells, electron-rich conjugated molecules and electron-poor conjugated molecules need to be assembled into segregated structures for efficient charge separation and charge-carrier transport.[3] Yet, there are no general approaches to spontaneously assemble electron-rich π-conjugated molecules and electron-poor π-conjugated molecules into segregated structures.[4]

Aromatic hydrocarbons form co-crystals with aromatic fluorocarbons.[5] Aliphatic fluorocarbons, on the other hand, will not co-crystallize with aliphatic hydrocarbons.[6] We reasoned that if we equip electron-rich conjugated π-systems with electron-donating aliphatic hydrocarbon side chains and electron-poor conjugated π-systems with electron-withdrawing fluorocarbon side chains, then the mutual phobicity of the side chains will drive the molecular assembly and result in structures with segregated domains of electron-rich conjugated units and electron-poor conjugated units. As a proof of principle, we report the spontaneous assembly of dyads containing naphthalimides with fluorocarbon side chains and naphthyl ethers with hydrocarbon side chains into segregated structures.

We synthesized molecules **1–6**, Chart 1, using established synthetic protocols (see ESI†) in excellent yields. In molecules **1**, **2**, **4**, and **6**, the electron-deficient naphthalimide is linked to the electron-rich naphthyl moiety through a rigid linker; molecules **3** and **5** have flexible glycol linkers. All of the compounds were crystallized and their crystal structures were determined from single crystal X-ray diffraction data.‡

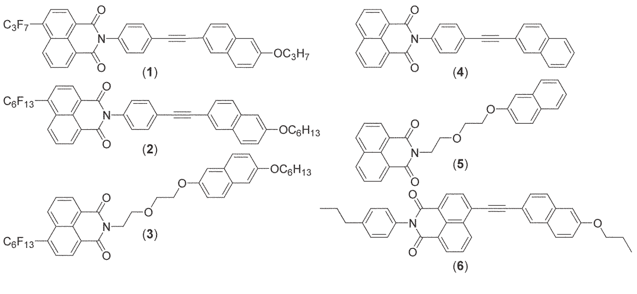

Chart 1

The packing of molecule **1** has three distinct characteristics: (a) perfluoropropyl chains and the propyl chains pack in separate domains, (b) between two dyads, the phenyl ring of the linker interacts with the naphthalimide moiety and with the naphthyl ether moiety through edge-to-face interactions, and (c) naphthalimides stack in the face-to-face geometry along the *a*-axis with a plane-to-plane distance of 3.534 Å and an offset angle of 46°; the angle between the planes is 0° (see Fig. 1a).§ The rigid linker produces a nearly coplanar arrangement between the naphthalimide and naphthyl ends of the molecule. The crystal structure and packing of molecule **2**, which has hexyl/perfluorohexyl side chains, is analogous to that of molecule **1** but with a tighter packing.¶ The plane-to-plane stacking distance is 3.509 Å, with an offset angle of 41°. It is noteworthy that while there are no face-to-face interactions between the electron-deficient naphthalimide and the electron-rich naphthyl ether in **1** and **2**, a close contact distance of 2.520 Å for **1** and 2.513 Å for **2** is observed between the carbonyl oxygen of the naphthalimide and the hydrogen of the neighboring naphthyl ether.

In the crystal structure of molecule **3**, which has a flexible linker, the naphthalimide units stack in the face-to-face geometry along the *b*-axis at a plane-to-plane distance of 3.566 Å with an offset angle of 41° (Fig. 2a).∥ The naphthyl ethers, on the other hand, pack in the herringbone-type arrangement—a configuration observed with the flexible linker but not with the rigid linker. Much like in **1** and **2**, the perfluorohexyl chains and the hexyl chains segregate into separate domains. This enforces the segregation of naphthalimide and naphthyl ether moieties (Fig. 2b). A close contact distance of 2.504 Å is observed between the carbonyl oxygen of the naphthalimide and hydrogen on the nearest naphthyl ether neighbor.

Also noteworthy is the packing of naphthalimide stacks in the crystal structures of molecule **1**, **2** and **3**. Generally, two columns of aromatic stacks pack in such a way that one column is canted with respect to the other; this is the herringbone arrangement between the columns. In these structures, however, the naphthalimide columns are parallel, with rows of naphthalimide packed in a face-to-face offset arrangement (Fig. 2c). We believe that this arrangement is enforced by the favorable packing of the fluorocarbon side chains.

In order to discern the role of the mutual phobicity of the side chains on the packing, we synthesized molecules **4**,** **5**†† and **6**.‡‡

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† Electronic supplementary information (ESI) available: Synthesis, crystallization procedures and characterization data for molecules **1–6**; calculated electrostatic potential surfaces of molecules **2–6**. See DOI: 10.1039/b610565c

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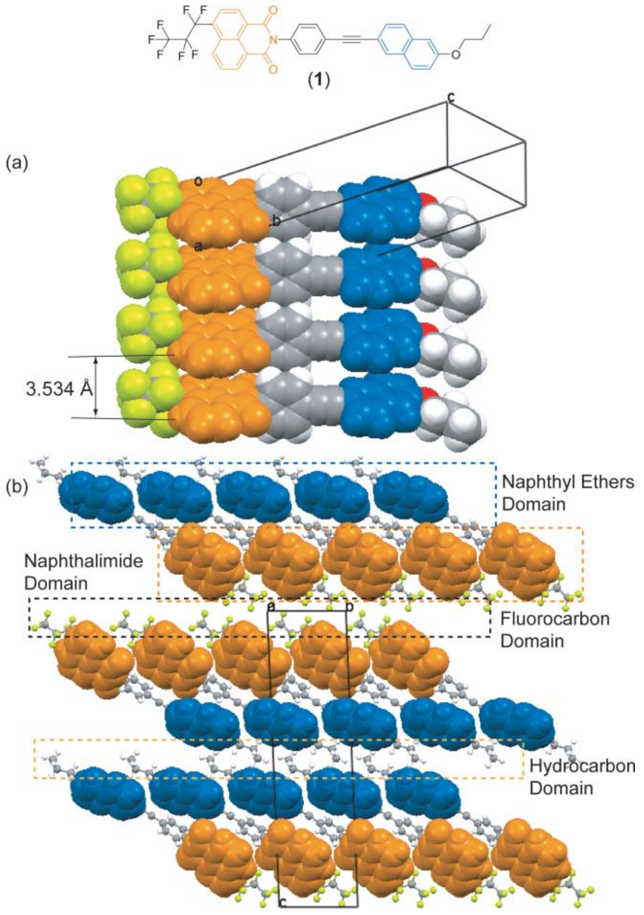

Fig. 1 (a) Illustration of the packing of the naphthalimide and naphthyl ether stacks in the crystal structure of molecule **1** and (b) illustration of the segregation of the naphthalimide and naphthyl ether units into separate domains. The disorder in the fluorocarbon chain is not shown for clarity.

We have also synthesized a molecule analogous to molecule **3** having hexyloxy chains at both ends (see ESI†). Thus far, we have not been able to obtain single crystals of this molecule suitable for X-ray diffraction. A common, dominant packing feature of the structures of **4**, **5** and **6** is the face-to-edge interaction between the naphthyl ether and the naphthalimide units (see Fig. 3); these interactions are absent in the structures of **1**, **2** and **3**. In addition to these naphthalimide–naphthyl ether interactions, there are also naphthalimide–naphthalimide and naphthyl ether–naphthyl ether interactions. These structures clearly indicate that the segregated assemblies obtained in molecules **1–3** are due to the innate phobicity of the aliphatic fluorocarbon–hydrocarbon side chains. Calculations of the electrostatic potential surfaces of molecules **4–6** support the packing motifs observed in these molecules (see ESI†).

In summary, we have shown that mutually phobic aliphatic hydrocarbon–fluorocarbon interactions can be used for spontaneous organization of electron-rich π-conjugated molecules and electron-poor π-conjugated molecules into phase-segregated assemblies. We believe that our approach will have implications in the creation of heterojunctions in photovoltaic devices. We are currently pursuing the use of these interactions in polymeric systems and those results will be reported in due course.

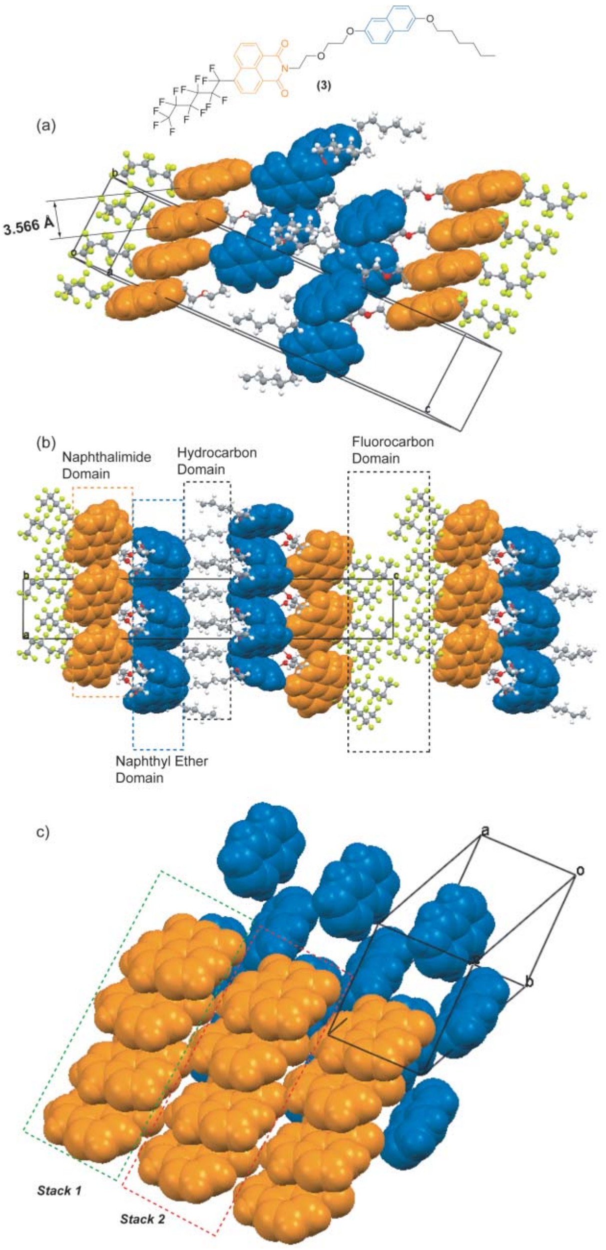

Fig. 2 (a) Illustration of the packing of the naphthalimide and naphthyl ether units in the crystal structure of molecule **3**. The disorder in the fluorocarbon side-chain is not shown for clarity. (b) Illustration of the segregation of the naphthalimide and naphthyl ether units into separate domains. (c) Illustration of the packing of the naphthalimide stacks in the crystal structure of **3**. The side chains and the linkers have been omitted for clarity. A similar packing is observed in molecules **1** and **2**.

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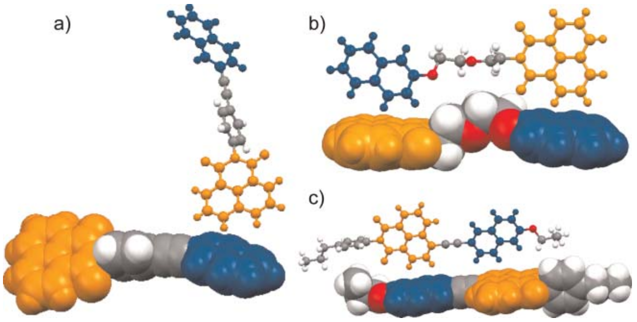

Fig. 3 Illustration of the edge-to-face packing observed between the naphthalimide and naphthyl ether units in the crystal structures of (a) molecule **4**, (b) molecule **5** and (c) molecule **6**.

Notes and references

‡ X-Ray data were collected using a Nonius kappa-CCD diffractometer with Mo-Kα (λ = 0.71073 Å) as the incident radiation. Structures were solved using SIR 97 or SIR 92 and were refined by full-matrix least-squares on F_o^2 using SHELXL97.

§ Crystal data for **1**: $C_{36}H_{22}F_7N_1O_3$, M = 649.55, triclinic, $P\bar{1}$ (2), a = 5.6784(8) Å, b = 8.4377(11) Å, c = 31.313(5) Å, α = 87.186(6)°, β = 87.102(5)°, γ = 79.417(8)°, V = 1471.6 Å^3, Z = 2, ρ = 1.466 g cm^{-3}, μ = 0.123 mm^{-1}, T = 293 K, λ(Mo-Kα) = 0.71073 Å, data/parameters = 5147/469, converging to R_1 = 0.0924, wR_2 = 0.1918 (on 2667 $I > 2\sigma(I)$ observed data); R_1 = 0.1842, wR_2 = 0.2428 (all data), residual electron density: 0.337 e Å^{-3}.

¶ Crystal data for **2**: $C_{42}H_{28}F_{13}N_1O_3$, M = 841.65, triclinic, $P\bar{1}$ (2), a = 5.8313(3) Å, b = 8.9482(5) Å, c = 36.8720(19) Å, α = 90.655(2)°, β = 91.406(2)°, γ = 104.355(2)°, V = 1863.03(17) Å^3, Z = 2, ρ = 1.5 g cm^{-3}, μ = 0.138 mm^{-1}, T = 293 K, λ(Mo-Kα) = 0.71073 Å, data/parameters = 6363/587, converging to R_1 = 0.1008, wR_2 = 0.2332 (on 3251 $I > 2\sigma(I)$ observed data); R_1 = 0.1775, wR_2 = 0.2773 (all data), residual electron density: 0.372 e Å^{-3}.

‖ Crystal data for **3**: $C_{38}H_{32}F_{13}N_1O_5$, M = 829.65, triclinic, $P\bar{1}$ (2), a = 7.9502(3) Å, b = 9.5259(4) Å, c = 49.289(2) Å, α = 88.7490(10)°, β = 90.2360(10)°, γ = 87.669(2)°, V = 3728.8(3) Å^3, Z = 4, ρ = 1.478 g cm^{-3}, μ = 0.14 mm^{-1}, T = 293 K, λ(Mo-Kα) = 0.71073 Å, data/parameters = 6097/1024, converging to R_1 = 0.1086, wR_2 = 0.3114 (on 4134, $I > 2\sigma(I)$ observed data); R_1 = 0.1477, wR_2 = 0.3534 (all data), residual electron density: 0.628 e Å^{-3}. The perfluorinated side chains are disordered. Refer to the ESI† for details.

** Crystal data for **4**: $C_{30}H_{17}N_1O_2$, M = 423.45, orthorhombic, $Pcab$ (61), a = 9.329(5) Å, b = 17.981(5) Å, c = 25.206(5) Å, V = 4244.95(27) Å^3, Z = 8, ρ = 1.325 g cm^{-3}, μ = 0.083 mm^{-1}, T = 293 K, λ(Mo-Kα) = 0.71073 Å, data/parameters = 4850/298, converging to R_1 = 0.0554, wR_2 = 0.1236 (on 2475 $I > \sigma(I)$ observed data); R_1 = 0.1310, wR_2 = 0.1538 (all data), residual electron density: 0.135 e Å^{-3}.

†† Crystal data for **5**: $C_{26}H_{21}N_1O_4$, M = 411.44, monoclinic, $P2_1/c$ (14), a = 12.140(5) Å, b = 5.718(5) Å, c = 29.183(5) Å, β = 96.673(5)°, V = 2012.06(23) Å^3, Z = 4, ρ = 1.358 g cm^{-3}, μ = 0.092 mm^{-1}, T = 293 K, λ(Mo-Kα) = 0.71073 Å, data/parameters = 3513/280, converging to R_1 = 0.0429, wR_2 = 0.1065 (on 2508 $I > \sigma(I)$ observed data); R_1 = 0.0655, wR_2 = 0.1211 (all data), residual electron density: 0.151 e Å^{-3}.

‡‡ Crystal data for **6**: $C_{36}H_{29}N_1O_3$, M = 523.62, monoclinic, $P2_1/c$ (14), a = 24.8660(4) Å, b = 5.2750(2) Å, c = 21.6140(11) Å, β = 101.028(1)°, V = 2782.72(6) Å^3, Z = 4, ρ = 1.25 g cm^{-3}, μ = 0.079 mm^{-1}, T = 293 K, λ(Mo-Kα) = 0.71073 Å, data/parameters = 4894/477, converging to R_1 = 0.0646, wR_2 = 0.1227 (on 2316, $I > 2\sigma(I)$ observed data); R_1 = 0.1623, wR_2 = 0.1642 (all data), residual electron density: 0.143 e Å^{-3}. CCDC 615872–615877. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b610565c

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