Electronic Supplementary Information

The art of stacking: structural folding and self-assembly of branched π-conjugation assisted by O–H···O and C–H···F hydrogen bonds

Ho Yong Lee, Andras Olasz, Maren Pink, Hyunsoo Park, and Dongwhan Lee*

Department of Chemistry, Indiana University,
800 East Kirkwood Avenue, Bloomington, Indiana 47405

Experimental Section

General Considerations. All reagents were obtained from commercial suppliers and used as received unless otherwise noted. The compound 4-(*tert*-butyl)-2-iodophenyl trifluoromethanesulfonate was prepared according to literature procedure.[1] All air-sensitive manipulations were carried out under nitrogen atmosphere in an M.Braun drybox or by standard Schlenk-line techniques.

Physical Measurements. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 300 MHz Varian Gemini 2000 or a 400 MHz Varian Inova NMR Spectrometer. Chemical shifts were reported versus tetramethylsilane and referenced to the residual solvent peaks. High-resolution chemical ionization (CI, using CH_4 as CI reagent) and electrospray ionization (ESI) mass spectra were obtained on a Thermo Electron Corporation MAT 95XP-Trap. FT-IR spectra were recorded on a Nicolet 510P FT-IR spectrometer with EZ OMNIC ESP software.

4-(*tert*-Butyl)-2-(3-hydroxyprop-1-yn-1-yl)phenyl trifluoromethanesulfonate (2). A round-bottom flask charged with 4-(*tert*-butyl)-2-iodophenyl trifluoromethanesulfonate (2.55 g, 6.24 mmol), *i*-Pr_2NH (20 mL), $PdCl_2(PPh_3)_2$ (151 mg, 0.215 mmol), CuI (71.1 mg, 0.373 mmol), and THF (40 mL) was purged with N_2. A portion of propargyl alcohol (0.80 mL) was delivered using syringe, and the reaction mixture was stirred for 8 h at r.t. under N_2. The crude reaction mixture was diluted with EtOAc (100 mL) and filtered through a Celite cake. Volatile fractions were removed under reduced pressure. Flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1, v/v) furnished **2** as a yellow oil (2.01 g, 5.97 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.54 (s, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 4.53 (d, J = 5.6 Hz, 2H), 2.09 (t, J = 6.4 Hz, 2H), 1.30 (s, 12H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 151.5, 147.7, 130.7, 127.2, 120.9, 120.2, 116.8, 93.9, 79.4, 51.4, 34.6, 31.0. FT-IR (thin film on NaCl, cm^{-1}): 3362, 2967, 2871, 2110, 1490, 1424, 1365, 1249, 1121, 1175, 1140, 1119, 1092, 1033, 984, 889, 858, 829, 790, 638. HRMS (ESI) calcd for $C_{14}H_{15}O_4F_3S$ $[M]^+$ 336.0643, found 336.0643.

3-(5-(*tert*-Butyl)-2-((triisopropylsilyl)ethynyl)phenyl)prop-2-yn-1-ol (3). A round-bottom flask charged with **2** (2.01 g, 5.97 mmol), *i*-Pr_2NH (10 mL), $Pd(dppf)Cl_2$ (251 mg, 0.343 mmol), CuI (81.1 mg, 0.425 mmol), and DMF (10 mL) was purged with N_2. A portion of ethynyltriisopropylsilane (1.5 mL) was delivered using syringe, and the reaction mixture was stirred for 24 h at 80 °C. After cooling to r.t., the crude reaction mixture was diluted with EtOAc (200 mL), and washed with water (100 mL × 5). The organic layer was dried over anhyd $MgSO_4$ and filtered. Volatile fractions were removed under reduced pressure and the residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to furnish **3** as a yellow oil (1.93 g, 5.23 mmol, 87%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.47 (s, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.4 Hz, 1H), 4.50 (d, J = 6.4 Hz, 2H), 1.62 (t, J = 6.4 Hz, 1H), 1.28 (s,

[1] Jiang, X.; Park, B. G.; Riddle, J. A.; Zhang, B. J.; Pink, M.; Lee, D. *Chem. Commun.* **2008**, 6028–6030.

9H), 1.14 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 151.3, 132.2, 129.1, 125.4, 124.8, 123.1, 105.2, 93.9, 90.2, 85.0, 51.7, 34.6, 30.9, 18.6, 11.2. FT-IR (thin film on NaCl, cm^{-1}): 3323, 2958, 2864, 2156, 1489, 1463, 1398, 1363, 1291, 1263, 1216, 1133, 1072, 1032, 996, 919, 883, 826, 757, 680. HRMS (ESI) calcd for $C_{24}H_{36}ONaSi$ $[M + Na]^+$ 391.2433, found 391.2444.

3-(5-(*tert*-Butyl)-2-ethynylphenyl)prop-2-yn-1-ol (4). To a stirred solution of **3** (1.93 g, 5.23 mmol) in THF (50 mL) at 0 °C under N_2 was added a THF solution of TBAF (1.0 M, 6.00 mL) over a period of 5 min using syringe. The reaction mixture was stirred for 5 h at r.t. under N_2, and concentrated under reduced pressure. The residual material was purified by flash column chromatography on SiO_2 (hexanes:EtOAc = 10:1, v/v) to furnish **4** as a yellow oil (1.01 g, 4.75 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.48 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.4 Hz, 1H), 4.55 (d, J = 6.4 Hz, 2H), 1.66 (bs, 1H), 1.29 (s, 9H). ^{1}3C NMR (100 MHz, $CDCl_3$, 298 K): δ 151.9, 132.3, 129.1, 125.5, 125.0, 121.5, 90.5, 84.5, 82.0, 80.4, 51.7, 34.7, 30.9. FT-IR (thin film on NaCl, cm^{-1}): 3287, 2962, 2905, 2867, 2107, 1489, 1464, 1394, 1362, 1263, 1231, 1202, 1133, 1096, 1031, 982, 894, 832, 742, 641. HRMS (CI) calcd for $C_{15}H_{16}O$ $[M]^+$ 212.1201, found 212.1189.

3,3′,3′′-[((2,4,6-Trifluorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tris(3-(tert-butyl)-benzene-6,1-diyl)]tris(prop-2-yn-1-ol) (1). A 50-mL tube equipped with a Teflon-lined screw cap was charged with 1,3,5-trifluoro-2,4,6-triiodobenzene (0.168 g, 0.329 mmol), **4** (0.298 g, 1.40 mmol), $PdCl_2(PPh_3)_2$ (12.1 mg, 0.017 mmol), CuI (9.12 mg, 0.047 mmol), and i-Pr_2NH (10 mL) in a glove box. The tube was sealed and removed from the glove box. The reaction mixture was stirred for 24 h at 80 °C. After cooling to r.t., the crude reaction mixture was diluted with EtOAc (50 mL) and filtered through a Celite cake. Volatile fractions were removed under reduced pressure. After preliminary purification step by flash column chromatography on SiO_2 (hexanes:EtOAc = 4:1 to 2:1, v/v), the inseparable mixture comprising streaking TLC spots with R_f values of 0.13–0.44 (hexanes : EtOAc = 2:1, v/v) was taken up into $CHCl_3$ (10 mL) and layered with hexanes (30 mL) to furnish **1** as a light-yellow crystalline solid (0.105 mg, 41 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.53 (m, 6H), 7.38 (d, J = 8.0 Hz, 3H), 4.60 (d, J = 6.0 Hz, 6H), 2.42 (t, J = 6.0 Hz, 3H), 1.32 (s, 27H). ^{1}3C NMR (100 MHz, $CDCl_3$, 298 K): δ 163.2, 160.6, 152.7, 132.0, 129.4, 125.9, 125.1, 121.8, 100.3, 98.9, 91.5, 84.2, 51.7, 35.0, 31.1. FT-IR (thin film on NaCl, cm^{-1}): 3361, 2962, 2906, 2867, 2220, 1606, 1494, 1456, 1395, 1363, 1266, 1224, 1115, 1083, 1031, 981, 948, 894, 858, 829, 739, 640. HRMS (ESI) calcd for $C_{51}H_{45}O_3NaF_3$ $[M + Na]^+$ 785.3219, found 785.3255.

X-ray Crystallographic Studies on 1U. A colorless block (approximate dimensions 0.15 × 0.12 × 0.08 mm^3) was selected and transferred to a Bruker APEX II Kappa Duo diffractometer under a stream of cold N_2. The crystals lose solvent and crystallinity rapidly and with no protection and cold handling turn into powder within seconds. Data were measured with an APEX II detector and at 150(2) K. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 6.0 cm. A collection strategy was calculated and complete data to a resolution of 0.82 Å with a redundancy of 4 were collected. Three major sections of frames were collected with 0.50° ω and ϕ scans. At high resolutions regions, Bragg diffraction was very weak. Thermal diffuse scattering was observed. Data to a resolution of 0.84 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9976 strong reflections from the actual data collection after integration (SAINT).[2] Intensity data were corrected for absorption (SADABS).[3]

[2] *SAINT*, Bruker Analytical X-Ray Systems, Madison, WI, current version.
[3] An empirical correction for absorption anisotropy. R. Blessing, *Acta Cryst. A51*, 33–38 (1995).

The space group $R\bar{3}$ was determined based on intensity statistics and systematic absences. The structure was solved using SIR-2004[4] and refined with SHELXL-97.[5] A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters with the exception of the chlorine and carbon atoms of the solvent chloroform. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0905$ and $wR2 = 0.2960$ (F^2, all data). The remaining electron density is located near the disordered solvent.

X-ray Crystallographic Studies on 1F. A colorless needle crystal (approximate dimensions $0.15 \times 0.05 \times 0.05$ mm^3) was placed onto the tip of a 0.05 mm diameter glass fiber and mounted on a Bruker APEX II Kappa Duo diffractometer equipped with an APEX II detector at 150(2) K. The data collection was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 30 seconds and a detector distance of 5.0 cm. A collection strategy was calculated and complete data to a resolution of 0.75 Å with a redundancy of 4 were collected using APEX2 software.[6] Six sections of frames were collected with 0.50° ω and ϕ scans. Data to a resolution of 0.80 Å were considered in the reduction. Final cell constants were calculated from the xyz centroids of 2155 strong reflections from the actual data collection after integration. The intensity data were corrected for absorption (SADABS).[3]

The space $P\bar{1}$ was determined based on intensity statistics and systematic absences. The structure was solved and refined using SHELXTL.[5] A direct methods solution was calculated, which provided all non-hydrogen atomic positions from the E-map. Full-matrix least squares / non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Approximately 55% of the unit cell volume comprises a large region of disordered solvents which could not be modeled as discrete atomic sites. PLATON/SQUEEZE[7] was thus employed to calculate the contribution to the diffraction from the solvent region, and it estimated a total count of 113 electrons per unit cell which could be assigned as 2 chloroform molecules. Using a set of solvent-free diffraction intensities, the final full matrix least squares refinement converged to $R1 = 0.1035$ and $wR2 = 0.2236$ (F^2, all data). The remaining electron density is minuscule and located on bonds.

Density Functional Theory (DFT) Calculations. Geometry optimizations were performed using the Jaguar 7.7 suite of *ab initio* quantum chemistry programs[8] at the B3LYP/6-31G** level of theory.[9,10] The energies of the optimized structures were re-evaluated by additional single-point calculations on optimized geometry using Dunning's correlation-consistent triple-ζ cc-pVTZ(-f) basis set.[11] Optimizations were carried out using the simplified model compounds **1′** and **5**, in which the *tert*-butyl groups on the phenyl rings of the parent system **1** were replaced by methyl groups to render the calculations computationally tractable. Absolute energies of monomers, **1′** and **5**, were calculated on frozen geometries obtained from the optimized dimers, $(\mathbf{1'})_2$ and $(\mathbf{5})_2$,

[4] *Sir2004*, A Program for Automatic Solution and Refinement of Crystal Structures. M. C. Burla, R. Caliandro, M. Carnalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Sagna. Version 1.0 (2004).
[5] A short history of *SHELX*. G. M. Sheldrick, *Acta Cryst. A64*, 112 –122 (2008).
[6] *APEX2*, Bruker Analytical X-Ray Systems, Madison, WI, 2009.
[7] Single-crystal structure validation with the program *PLATON*. A.L. Spek, *J. Appl. Cryst. 36*, 7–13 (2003).
[8] *Jaguar*, v7.7; Schrödinger, LLC: New York, 2010.
[9] Becke, A. D., *J. Chem. Phys.* **1993**, *98*, 5648–5652.
[10] Lee, C.; Yang, W.; Parr, R. G., *Physical Review B: Condensed Matter and Materials Physics* **1988**, *37*, 785–789.
[11] Dunning, T. H., Jr., *J. Chem. Phys.* **1989**, *90*, 1007–1023.

respectively. Interaction energies were calculated as the difference of refined energies between twice the monomer and the dimer. No further refinement of the interaction energies was carried out (such as BSSE or solvent corrections) since the relevant information is the difference of interaction energies where the effect of refinements are anticipated to cancel out.

Optimized geometries maintain the *pseudo*-D_{3d} symmetry of the dimer. In $(\mathbf{1}')_2$, the C–F$\cdots$H contacts are 2.45 Å apart from each other on average, which is 0.174 Å *shorter* than the sum of van der Waals radii of F and H. In $(\mathbf{5})_2$, the C–H$\cdots$H contacts have an average distance of 2.69 Å, which is 0.29 Å *longer* than the sum of van der Waals radii. Energy evaluation further supports the hypothesis that C–F$\cdots$H contacts contribute to the thermodynamic stability of the dimer. While $(\mathbf{5})_2$ is stabilized by an interaction energy of 34.6 kcal mol^{-1} (referenced to the monomeric $\mathbf{5}$), $(\mathbf{1}')_2$ is stabilized by 42.0 kcal mol^{-1} (referenced to monomeric $\mathbf{1}'$). Divided by the number of C–F$\cdots$H contacts, each contact contributes to the overall dimer stability by 1.2 kcal mol^{-1}.

Table S1. Energy components of the calculated structures.

DFT model	E(SCF) cc-pVTZ(-f) eV
$\mathbf{(1')}_2$	–116589.021
$\mathbf{(5)}_2$	–100381.293
$\mathbf{1'}$	–58293.600
5	–50189.897

Table S2. Cartesian coordinates (in Å) of the DFT model $\mathbf{(1')}_2$.

Atom	x	y	z
F	–1.969200501	–1.849797235	3.888945535
C	–0.989807235	–0.93589215	3.912332709
C	0.338723954	–1.384446443	3.913030032
C	0.667080653	–2.764882231	3.829718779
C	0.948484913	–3.938593324	3.705161286
C	1.274864194	–5.315363546	3.5271896
C	1.286895969	–5.896472053	2.230447073
C	1.621809311	–7.254606358	2.088006636
H	1.629296169	–7.67890183	1.088432875
C	1.943454965	–8.053655262	3.184800605
C	1.928241463	–7.465830894	4.460398793
H	2.178952693	–8.067502037	5.33047815
C	1.600265377	–6.126438555	4.628833873
H	1.593996985	–5.684909455	5.620256775
C	2.289990793	–9.513307367	3.013189265
C	0.978197403	–5.119458762	1.078065096
C	0.719718718	–4.464287479	0.092782001
C	0.444059834	–3.618619476	–1.071079091
H	1.285504465	–3.675410802	–1.774515031
H	–0.440882647	–3.982058162	–1.604960132
O	0.179684001	–2.263819285	–0.724717636
H	0.95363954	–1.88324872	–0.234244576
F	–0.601507558	2.65038893	3.937205297
C	–0.298737405	1.345051626	3.936632797
C	–1.351280914	0.419799213	3.913263029
C	–2.708104449	0.834584776	3.835086134
C	–3.858890987	1.199969667	3.717191331
C	–5.205904148	1.632468427	3.541435615
C	–5.717647354	1.900976876	2.242802224
C	–7.051468696	2.322285088	2.103326494
H	–7.425718364	2.520191574	1.103337471
C	–7.890838284	2.485558922	3.204722369
C	–7.372637832	2.215084149	4.481567463
H	–8.010014986	2.332292791	5.354403599
C	–6.058212474	1.79797018	4.647071109

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Table Continued

Atom	x	y	z
H	–5.669930482	1.591052146	5.639199075
C	–9.317440628	2.950819257	3.035053735
C	–4.903180528	1.738186231	1.086324027
C	–4.217963631	1.599769446	0.097220538
C	–3.361777186	1.38183639	–1.070905066
H	–3.848765258	0.676809079	–1.757994615
H	–3.224452547	2.318661005	–1.621937967
O	–2.0607243	0.91815822	–0.726654595
H	–2.131406133	0.056465279	–0.239177365
F	2.61353932	–0.78352065	3.936458075
C	1.331510071	–0.393300068	3.936523905
C	1.055902633	0.980924731	3.933471899
C	2.084875126	1.957108694	3.862285206
C	2.95627766	2.791492335	3.741087702
C	3.976743678	3.766995015	3.550255662
C	4.455005114	4.066231445	2.246519337
C	5.458005243	5.038882613	2.09145066
H	5.810078958	5.2580972	1.088662996
C	5.998744859	5.721411426	3.180461425
C	5.514831568	5.416375147	4.462789828
H	5.918685584	5.938567606	5.326512356
C	4.525395092	4.458686282	4.644316569
H	4.158041035	4.232560754	5.64018824
C	7.082364151	6.756096431	2.990770166
C	3.92387802	3.407087953	1.100785531
C	3.475971776	2.857680873	0.118389511
C	2.871968918	2.204097136	–1.045674593
H	2.504815713	2.967762668	–1.744472145
H	3.624106543	1.617207417	–1.584109459
O	1.824718874	1.301516572	–0.70525628
H	1.107273276	1.780071187	–0.21301817
F	1.941961555	1.866564563	–3.897331247
C	0.966137516	0.94831447	–3.913804499
C	–0.363698097	1.394054124	–3.907986587
C	–0.689846369	2.774703471	–3.821772394
C	–0.958326954	3.950889737	–3.695345111
C	–1.271760064	5.329156844	–3.508047992
C	–1.293828598	5.898068884	–2.20619259
C	–1.610243606	7.259684135	–2.055855596
H	–1.62522368	7.674726561	–1.052561604
C	–1.905005476	8.0734837	–3.149525919
C	–1.881933027	7.497111508	–4.430149081
H	–2.112474348	8.110061266	–5.297918178
C	–1.571118061	6.154628376	–4.606218643

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Table Continued

Atom	x	y	z
H	–1.558245505	5.722023705	–5.601529663
C	–2.231231393	9.536565583	–2.96869937
C	–1.01245212	5.105964944	–1.057123464
C	–0.778341411	4.436906662	–0.075046431
C	–0.527674243	3.576566	1.083716148
H	–1.391826684	3.610760511	1.760714561
H	0.334240812	3.944577781	1.650740886
O	–0.233349904	2.230637763	0.725438816
H	–0.996358976	1.838865859	0.224036094
F	0.588990394	–2.638071566	–3.925995274
C	0.282842083	–1.33371618	–3.92875241
C	1.332902669	–0.405856328	–3.910447935
C	2.690636338	–0.817949272	–3.82957659
C	3.8432182	–1.176372183	–3.705236738
C	5.192989841	–1.599778508	–3.525006671
C	5.702075521	–1.870207284	–2.225373336
C	7.041058637	–2.27415025	–2.082238739
H	7.413466377	–2.472203849	–1.081576954
C	7.888053005	–2.418927287	–3.180265675
C	7.372119738	–2.148633073	–4.458155463
H	8.015408904	–2.251609024	–5.328461581
C	6.052802134	–1.748504701	–4.627619368
H	5.666769518	–1.540474193	–5.620370964
C	9.320672692	–2.863900019	–3.005721109
C	4.880873777	–1.724337311	–1.07132707
C	4.189375294	–1.596657375	–0.085344645
C	3.324923614	–1.383821268	1.077815109
H	3.793973571	–0.658717627	1.756682916
H	3.208577817	–2.316305941	1.640867188
O	2.014482306	–0.955687424	0.724386551
H	2.064016939	–0.09409477	0.233149806
F	–2.636640426	0.785603492	–3.928416292
C	–1.353365127	0.400051375	–3.930149009
C	–1.07271225	–0.973190708	–3.927831587
C	–2.098295862	–1.953648341	–3.865494744
C	–2.966743817	–2.793315966	–3.75868523
C	–3.983270315	–3.777216435	–3.590238603
C	–4.467972061	–4.098896913	–2.293556181
C	–5.464442595	–5.081070654	–2.159354308
H	–5.820822982	–5.31919036	–1.162164905
C	–5.993261355	–5.750255873	–3.26253917
C	–5.504254628	–5.422047514	–4.537194447
H	–5.899561837	–5.934470165	–5.410687423
C	–4.520268626	–4.455076127	–4.69917306

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Table Continued

Atom	x	y	z
H	–4.147790281	–4.211516449	–5.688843937
C	–7.070891197	–6.795268941	–3.095638913
C	–3.949357667	–3.452215807	–1.134858116
C	–3.511350596	–2.910791371	–0.143589066
C	–2.921344887	–2.260430381	1.030071267
H	–2.542076172	–3.024855602	1.721830907
H	–3.684567049	–1.692519441	1.573419286
O	–1.888360229	–1.338130389	0.701031472
H	–1.158844101	–1.804212726	0.21550999
H	–10.01410821	2.306316328	3.582362884
H	–9.615347144	2.953469966	1.983164761
H	–9.449759397	3.968795672	3.421077682
H	–8.032046325	–6.438111491	–3.484766556
H	–7.215466239	–7.056551129	–2.043909431
H	–6.824041927	–7.712800187	–3.641037391
H	1.50031684	–10.15733734	3.418725055
H	2.421441326	–9.772813573	1.959345129
H	3.215164547	–9.767254295	3.542245233
H	9.470282966	–3.877538206	–3.396862717
H	10.01058299	–2.205922837	–3.545490857
H	9.613066184	–2.868357635	–1.952276311
H	8.040224406	6.404479842	3.392812222
H	7.231948063	6.989571308	1.933204454
H	6.837939357	7.688567215	3.5114751
H	–1.424711155	10.17179458	–3.354493182
H	–2.375782071	9.787394182	–1.914470058
H	–3.143356465	9.810685536	–3.510133713

Table S3. Cartesian coordinates (in Å) of the DFT model $\mathbf{(5)}_2$.

Atom	x	y	z
C	–1.021895135	–0.981767561	3.908126777
C	0.319951487	–1.389618096	3.899978204
C	0.651764591	–2.77566424	3.815687312
C	0.939138635	–3.948944149	3.692742566
C	1.292213977	–5.316167489	3.501636273
C	1.136173952	–5.938004059	2.232548759
C	1.527588317	–7.278413627	2.072033789
H	1.41247	–7.733785034	1.092844297
C	2.062934943	–8.021024899	3.124296438
C	2.206997683	–7.395689785	4.372444822
H	2.626939911	–7.953334152	5.205849394
C	1.8299537	–6.072100108	4.557455034

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Table Continued

Atom	x	y	z
H	1.954004234	–5.598032061	5.526012608
C	2.472589995	–9.462016394	2.933717908
C	0.618375046	–5.20907672	1.123113997
C	0.189077787	–4.585441151	0.17773533
C	–0.263577506	–3.759041101	–0.94593083
H	0.374783716	–3.964555224	–1.819600493
H	–1.28667654	–4.026905048	–1.231128449
O	–0.272367369	–2.369882799	–0.651003275
H	0.599078716	–2.098227159	–0.262862314
C	–0.330940994	1.340678185	3.903112942
C	–1.355101059	0.382029782	3.896662439
C	–2.720747756	0.790290245	3.808550247
C	–3.876170551	1.139800894	3.675506929
C	–5.231924754	1.532625321	3.476971853
C	–5.679013983	1.988124009	2.206137977
C	–7.029342404	2.339988689	2.037986186
H	–7.354640471	2.67711608	1.058161166
C	–7.948336068	2.256303465	3.083867608
C	–7.493162655	1.806677661	4.333509732
H	–8.192823913	1.728166875	5.161971368
C	–6.163892099	1.453296464	4.526603407
H	–5.826071405	1.101701251	5.496290705
C	–9.394081688	2.644961661	2.884843728
C	–4.781575893	2.063126709	1.102114926
C	–4.019864367	2.115875097	0.161882889
C	–3.069377253	2.088617905	–0.95387338
H	–3.554237565	1.622532426	–1.825880838
H	–2.795072058	3.106661266	–1.249844668
O	–1.859865191	1.415498723	–0.638171754
H	–2.060398067	0.523437184	–0.254205772
C	1.335445634	–0.41983551	3.90789392
C	1.016960253	0.946132417	3.899506247
C	2.051211521	1.926809554	3.819540483
C	2.928197363	2.757821269	3.698896177
C	3.941867015	3.742321839	3.515092802
C	4.57142853	3.911727499	2.251673804
C	5.546174748	4.913163981	2.09888288
H	6.008919686	5.035723783	1.124052052
C	5.917096877	5.747740211	3.153326178
C	5.289113779	5.567504324	4.395755903
H	5.558673639	6.210066418	5.23032872
C	4.322847959	4.585672978	4.57358843
H	3.840135612	4.460690495	5.537634113
C	6.971228777	6.813902179	2.971497962

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Table Continued

Atom	x	y	z
C	4.20185285	3.099948052	1.140305027
C	3.875626752	2.416134271	0.195074416
C	3.383770512	1.608877814	–0.926349118
H	3.243625036	2.259127236	–1.804074335
H	4.124055243	0.852398085	–1.207469301
O	2.183481656	0.911997618	–0.625778541
H	1.516972081	1.539525758	–0.245432406
C	0.988099378	0.955277704	–3.912484088
C	–0.35443523	1.361662569	–3.910768381
C	–0.683366433	2.749127089	–3.839211591
C	–0.95037522	3.927789093	–3.721842664
C	–1.278654744	5.301140652	–3.531194537
C	–1.098859182	5.92163104	–2.264703335
C	–1.459188707	7.270777939	–2.10398668
H	–1.32625282	7.725683179	–1.126819045
C	–1.985276969	8.023246227	–3.154004451
C	–2.153485918	7.398971515	–4.39978707
H	–2.566442785	7.964879994	–5.231061657
C	–1.807649016	6.066582546	–4.584782292
H	–1.948946059	5.593111912	–5.55122722
C	–2.358242915	9.474363752	–2.963478883
C	–0.586701391	5.185103079	–1.157685699
C	–0.160752864	4.56240834	–0.20977065
C	0.287095947	3.742333165	0.920255482
H	–0.357914318	3.948560667	1.788898043
H	1.307270287	4.015232962	1.210428039
O	0.303551673	2.352660497	0.631618807
H	–0.568041277	2.075659422	0.247940624
C	0.298818171	–1.368609863	–3.890685086
C	1.321750849	–0.408623805	–3.892628968
C	2.689480927	–0.808691547	–3.807889691
C	3.851233082	–1.13913164	–3.686342577
C	5.215759634	–1.504288473	–3.500485933
C	5.683484427	–1.955143624	–2.236276971
C	7.043421467	–2.272709103	–2.08013759
H	7.384658764	–2.60565332	–1.104316395
C	7.952436443	–2.15955654	–3.131879112
C	7.476703614	–1.716393599	–4.375834729
H	8.168195738	–1.615713255	–5.208737994
C	6.137054018	–1.396117722	–4.557011498
H	5.783070892	–1.046726845	–5.521682139
C	9.409736785	–2.509259087	–2.944601004
C	4.796348795	–2.05399098	–1.126028281
C	4.042474645	–2.122360416	–0.181003977

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Table Continued

Atom	x	y	z
C	3.095964157	–2.106597025	0.938818687
H	3.581069808	–1.645425523	1.813324845
H	2.824451491	–3.12728008	1.227993639
O	1.884009998	–1.435495541	0.630033647
H	2.084818703	–0.542184016	0.249140209
C	–1.368722544	0.39077203	–3.911021948
C	–1.049159275	–0.975104192	–3.888455799
C	–2.08506902	–1.953632909	–3.795142226
C	–2.963820485	–2.780734672	–3.662108432
C	–3.980492733	–3.759091958	–3.461376897
C	–4.592920769	–3.92265402	–2.188599765
C	–5.575250982	–4.914202808	–2.02059043
H	–6.025159223	–5.031220285	–1.039044255
C	–5.969813537	–5.745636957	–3.069277774
C	–5.35715067	–5.572449282	–4.320080364
H	–5.643904498	–6.213268378	–5.15017291
C	–4.384275688	–4.600078238	–4.512597444
H	–3.915032759	–4.480144411	–5.483908632
C	–7.034209671	–6.799492084	–2.873462986
C	–4.199529145	–3.112471883	–1.084826171
C	–3.852063792	–2.428793558	–0.147437694
C	–3.331796225	–1.622497176	0.960279257
H	–3.169011025	–2.274360016	1.83279155
H	–4.063848482	–0.865829975	1.261423299
O	–2.138592509	–0.928145809	0.627347609
H	–1.480603087	–1.556945819	0.233701402
H	–10.06948392	1.901584088	3.321982577
H	–9.640206754	2.742001111	1.823993793
H	–9.61662505	3.605031583	3.36634581
H	–7.979272734	–6.500996357	–3.343886717
H	–7.233283585	–6.975958247	–1.812936522
H	–6.737982939	–7.752388941	–3.32502352
H	1.753942048	–10.14420651	3.404198793
H	2.532813054	–9.724492186	1.874079532
H	3.449473341	–9.660803671	3.387565263
H	9.652395822	–3.467016612	–3.420997606
H	10.06109976	–1.751987906	–3.394018731
H	9.66891954	–2.591848117	–1.885575542
H	7.913293982	6.526541029	3.454268615
H	7.182678977	6.992016527	1.913662394
H	6.657433139	7.76358397	3.418095307
H	–1.624024427	10.1379305	–3.436596396
H	–2.408542221	9.739144205	–1.903879456
H	–3.33118278	9.697481089	–3.414425938

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Table Continued

Atom	x	y	z
H	2.373970312	–0.728605365	3.889614936
H	–0.582024289	2.394449468	3.879056129
H	–1.807887835	–1.726710962	3.89041751
H	0.551392019	–2.421728653	–3.859129429
H	–2.407575209	0.698444559	–3.896496624
H	1.773997628	1.70122158	–3.898063628

Table S4. Cartesian coordinates (in Å) of the DFT model **1′**.

Atom	x	y	z
F	–1.969200501	–1.849797235	3.888945535
C	–0.989807235	–0.93589215	3.912332709
C	0.338723954	–1.384446443	3.913030032
C	0.667080653	–2.764882231	3.829718779
C	0.948484913	–3.938593324	3.705161286
C	1.274864194	–5.315363546	3.5271896
C	1.286895969	–5.896472053	2.230447073
C	1.621809311	–7.254606358	2.088006636
H	1.629296169	–7.67890183	1.088432875
C	1.943454965	–8.053655262	3.184800605
C	1.928241463	–7.465830893	4.460398793
H	2.178952692	–8.067502037	5.33047815
C	1.600265377	–6.126438555	4.628833873
H	1.593996985	–5.684909455	5.620256775
C	2.289990793	–9.513307367	3.013189264
C	0.978197403	–5.119458762	1.078065095
C	0.719718718	–4.464287479	0.092782001
C	0.444059834	–3.618619476	–1.071079091
H	1.285504465	–3.675410802	–1.774515031
H	–0.440882647	–3.982058162	–1.604960132
O	0.179684001	–2.263819285	–0.724717636
H	0.95363954	–1.88324872	–0.234244576
F	–0.601507558	2.65038893	3.937205297
C	–0.298737405	1.345051626	3.936632797
C	–1.351280914	0.419799213	3.913263028
C	–2.708104449	0.834584776	3.835086134
C	–3.858890987	1.199969667	3.717191331
C	–5.205904148	1.632468427	3.541435615
C	–5.717647354	1.900976876	2.242802224
C	–7.051468696	2.322285088	2.103326494
H	–7.425718364	2.520191574	1.103337471
C	–7.890838284	2.485558922	3.204722369
C	–7.372637832	2.215084149	4.481567463

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Table Continued

Atom	x	y	z
H	–8.010014985	2.332292791	5.354403599
C	–6.058212474	1.79797018	4.647071109
H	–5.669930482	1.591052146	5.639199075
C	–9.317440628	2.950819256	3.035053735
C	–4.903180528	1.73818623	1.086324027
C	–4.217963631	1.599769446	0.097220537
C	–3.361777186	1.38183639	–1.070905066
H	–3.848765258	0.676809079	–1.757994615
H	–3.224452547	2.318661005	–1.621937967
O	–2.0607243	0.91815822	–0.726654595
H	–2.131406133	0.056465279	–0.239177365
F	2.61353932	–0.78352065	3.936458075
C	1.331510071	–0.393300068	3.936523905
C	1.055902633	0.980924731	3.933471899
C	2.084875126	1.957108694	3.862285206
C	2.95627766	2.791492335	3.741087702
C	3.976743678	3.766995015	3.550255662
C	4.455005114	4.066231445	2.246519337
C	5.458005243	5.038882613	2.09145066
H	5.810078958	5.2580972	1.088662996
C	5.998744859	5.721411426	3.180461425
C	5.514831568	5.416375147	4.462789828
H	5.918685584	5.938567606	5.326512356
C	4.525395092	4.458686282	4.644316569
H	4.158041035	4.232560754	5.64018824
C	7.082364151	6.756096431	2.990770166
C	3.92387802	3.407087953	1.100785531
C	3.475971776	2.857680873	0.118389511
C	2.871968918	2.204097136	–1.045674593
H	2.504815713	2.967762668	–1.744472145
H	3.624106543	1.617207417	–1.584109459
O	1.824718874	1.301516572	–0.70525628
H	1.107273276	1.780071187	–0.21301817
H	–10.01410821	2.306316328	3.582362884
H	–9.615347144	2.953469966	1.983164761
H	–9.449759397	3.968795672	3.421077682
H	1.50031684	–10.15733734	3.418725055
H	2.421441326	–9.772813573	1.959345129
H	3.215164547	–9.767254295	3.542245233
H	8.040224406	6.404479842	3.392812222
H	7.231948063	6.989571308	1.933204454
H	6.837939357	7.688567215	3.5114751

Table S5. Cartesian coordinates (in Å) of the DFT model **5**.

Atom	x	y	z
C	1.058966291	0.927026135	–4.043183656
C	–0.269240433	1.37947164	–4.029955494
C	–0.541214216	2.779306039	–3.933656218
C	–0.741753188	3.967807143	–3.787491031
C	–0.963014514	5.364245771	–3.605797553
C	–1.045687764	5.932681033	–2.306679573
C	–1.250486906	7.317538265	–2.176878414
H	–1.311667054	7.734428579	–1.177556
C	–1.373009053	8.155680621	–3.28442559
C	–1.296071549	7.580071297	–4.56137987
H	–1.394567863	8.211664891	–5.440182986
C	–1.094311842	6.214153702	–4.718223505
H	–1.035177581	5.780521032	–5.710852401
C	–1.558237004	9.645300583	–3.115946163
C	–0.929286915	5.129704718	–1.134270071
C	–0.831790168	4.479242396	–0.116925386
C	–0.721091191	3.623473811	1.070279203
H	–1.654963151	3.675710484	1.650564295
H	0.084957152	3.986719158	1.718646321
O	–0.410709716	2.274196007	0.755824474
H	–1.157472745	1.870032755	0.239702959
C	0.294394969	–1.368813066	–3.994343792
C	1.34957229	–0.444962626	–4.005665449
C	2.705703409	–0.881407052	–3.883488287
C	3.856192619	–1.229299971	–3.711321591
C	5.207586775	–1.624248854	–3.482043975
C	5.712044209	–1.77512422	–2.16222649
C	7.053722853	–2.15413768	–1.976177575
H	7.420512103	–2.260042994	–0.959790419
C	7.909277923	–2.390212823	–3.050699081
C	7.397717402	–2.239496056	–4.349222819
H	8.045966481	–2.415972381	–5.203551723
C	6.076654533	–1.865751986	–4.560414204
H	5.695419908	–1.749848024	–5.56965503
C	9.344204321	–2.806721659	–2.828946355
C	4.889085184	–1.541531977	–1.023600411
C	4.215859798	–1.350427804	–0.035649491
C	3.337588131	–1.094667785	1.109388639
H	3.751373703	–0.273694489	1.713181551
H	3.294079323	–1.981236819	1.75257291
O	2.003658677	–0.801937477	0.726556091
H	1.97976967	0.051938997	0.216982923
C	–1.315122582	0.443196722	–4.012814658
C	–1.039739744	–0.933180709	–3.982419649
C	–2.10257514	–1.879720648	–3.839790285

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Table Continued

Atom	x	y	z
C	–2.991673203	–2.687122063	–3.657838556
C	–4.026992842	–3.638724157	–3.411036907
C	–4.407705791	–3.982989111	–2.085194148
C	–5.423626684	–4.935516023	–1.885001747
H	–5.698101531	–5.185797418	–0.86493099
C	–6.075889076	–5.554167953	–2.950680093
C	–5.689615255	–5.206381856	–4.254131529
H	–6.179734478	–5.677996709	–5.102287495
C	–4.688183019	–4.270335273	–4.478682445
H	–4.399013167	–4.014656479	–5.491953916
C	–7.178990279	–6.55939989	–2.716146164
C	–3.780802742	–3.381238823	–0.957010192
C	–3.276525588	–2.879421908	0.022777372
C	–2.603838917	–2.239575445	1.156304156
H	–2.111650675	–3.008292252	1.770339383
H	–3.338661114	–1.732985981	1.792222083
O	–1.663136372	–1.255523555	0.752642836
H	–0.954139603	–1.685253926	0.204492136
H	–8.159376381	–6.135944623	–2.96826823
H	–7.215255121	–6.878841989	–1.671150705
H	–7.044297853	–7.451084865	–3.338229865
H	9.50493391	–3.849063341	–3.129713511
H	10.03345386	–2.192136554	–3.41836286
H	9.628986708	–2.717144122	–1.77727401
H	–0.60874932	10.178591	–3.247231197
H	–1.936879235	9.891421684	–2.120651602
H	–2.258521941	10.04718518	–3.854508343
H	0.510498629	–2.428597986	–3.950159229
H	–2.342249126	0.786258796	–3.98135232
H	1.869217899	1.646256544	–4.037304565

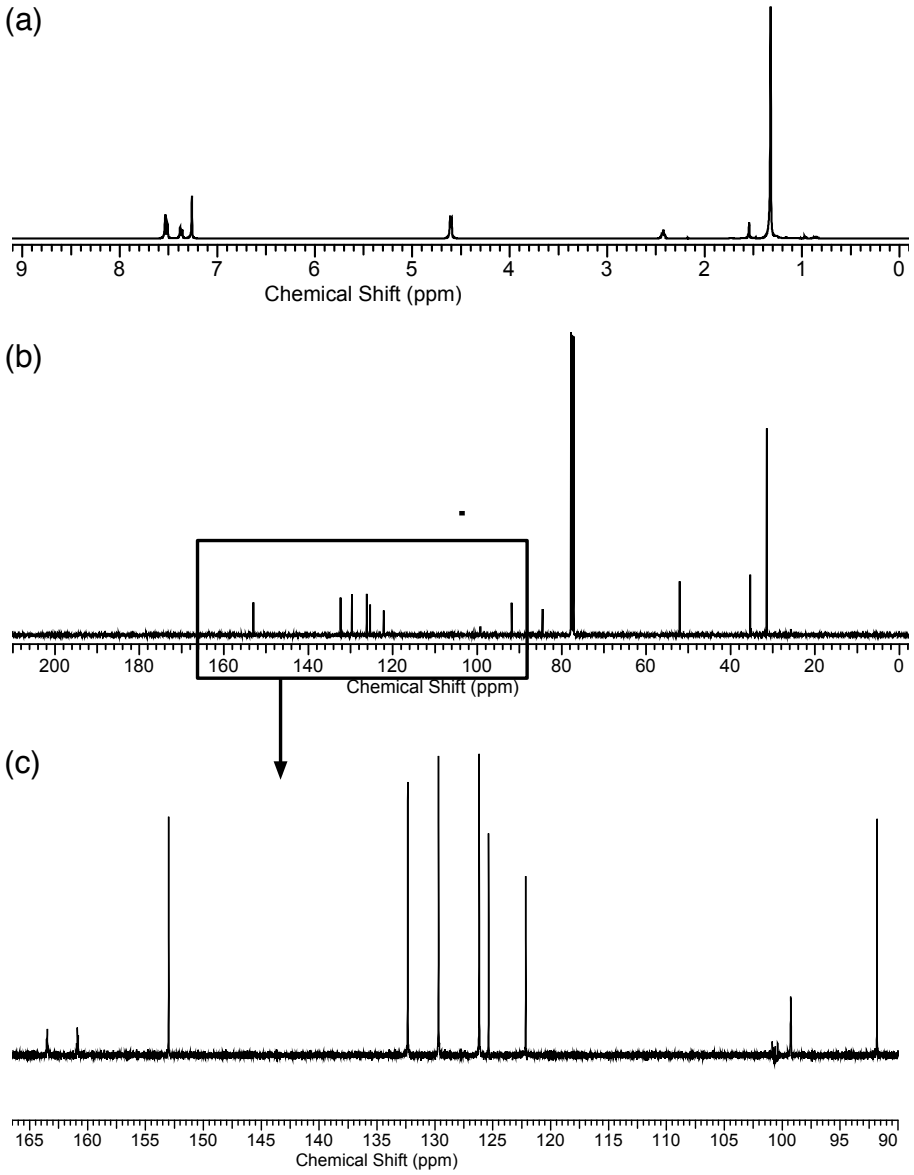

Fig. S1. (a) ^{1}H NMR spectra (400 MHz, $T = 298$ K), and (b) ^{13}C NMR spectra (100 MHz, $T = 298$ K) of **1** in in $CDCl_3$. In (c) is shown partial ^{13}C NMR spectra for the spectral window indicated with a box in (b).

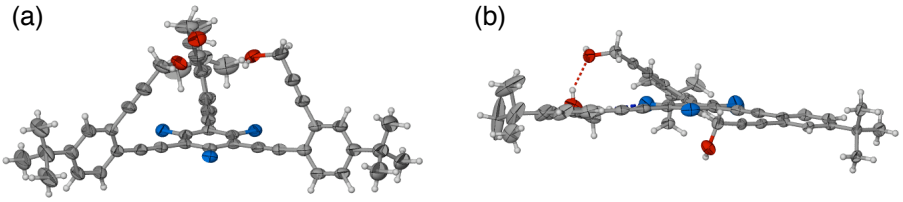

Fig. S2. X-ray structures of (a) **1U** and (b) **1F** with thermal ellipsoids at 50% probability, where O is red and F is blue. The O–H···O and C–H···F interactions are represented by red and blue dotted lines, respectively.

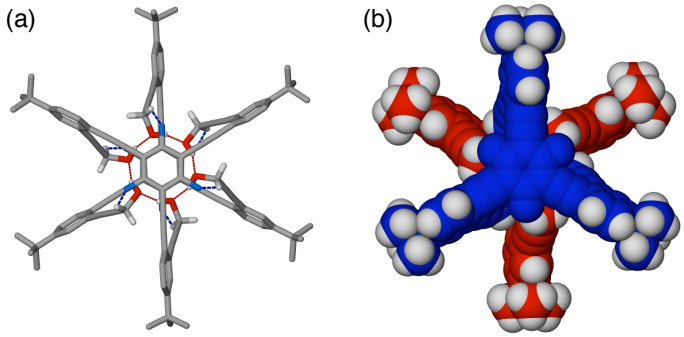

Fig. S3. (a) Capped stick and (b) space-filling representations (blue, top molecule; red, bottom molecule) of the solid-state structure of dimeric $(\mathbf{1U})_2$ generated using X-ray coordinates. The O–H···O and C–H···F interactions are represented by dotted lines.

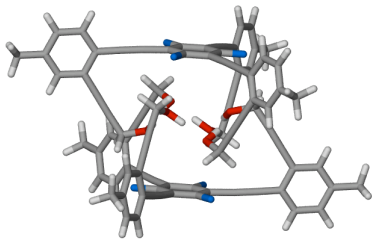

Fig. S4. Capped-stick representation of the DFT (B3LYP/6-31G**) geometry optimized model $(\mathbf{1}')_2$.

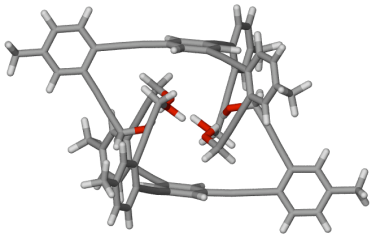

Fig. S5. Capped-stick representation of the DFT (B3LYP/6-31G**) geometry optimized model $(\mathbf{5})_2$.

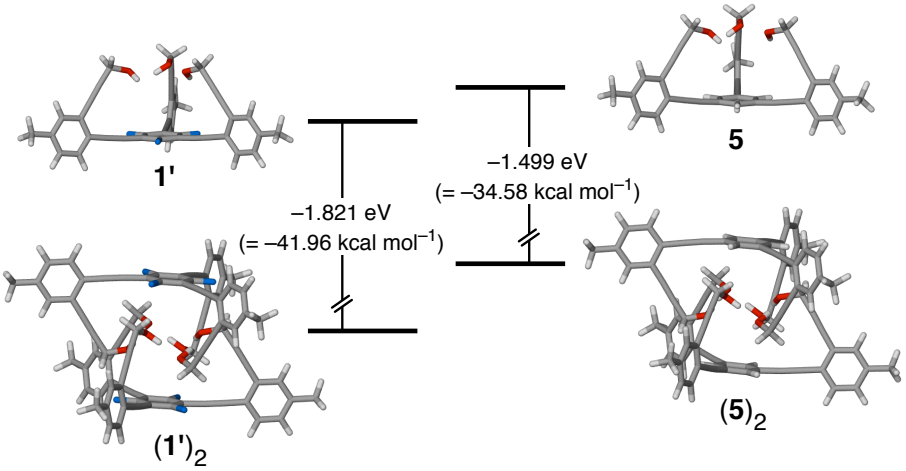

Fig. S6. Interaction energies of $(\mathbf{1}')_2$ and $(\mathbf{5})_2$ referenced to the corresponding monomers $\mathbf{1}'$ and $\mathbf{5}$, respectively.