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Electronic supplementary information

Controlling the self assembly of arene functionalised 2-aminopyrimidines by arene-perfluoroarene interaction and silver(I) complex formation

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Electronic energy (E_{el}), dipole moment ($|\mu|$), isotropic polarisability (α), Cartesian Coordinates, and MEP of compounds 4, 5, and 6:

compound	**4**	**5**	**6**
E_{el} / a.u.	-550.824221	-704.479307	-704.483211
$\|\mu\|$ / D	0.45	0.44	0.45
α / Bohr^3	—	202.03	213.25

Table S1: Electronic energies, dipole moments, and static isotropic polarisabilities of compounds **4-6**.

Figures S1-S3 show the color-coded MEP mapped on the molecular van-der-Waals surface (these pictures have been created with MOLDEN[1]). The pyrimidine ring is in always the upper part and in plane.

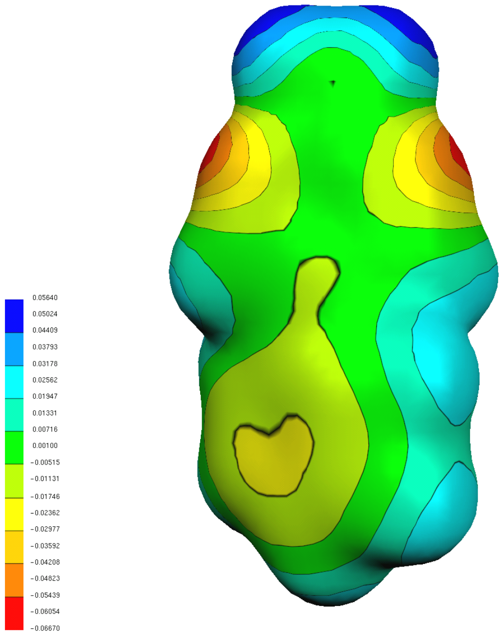

Figure 1: MEP of **4**, range: 0.056400 a.u.(blue) to -0.06700 a.u. (red).

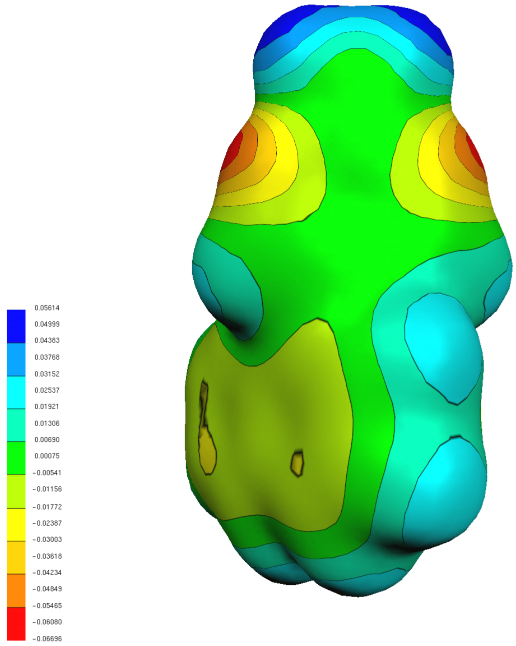

Figure 2: MEP of **5**, range: 0.05614 a.u.(blue) to -0.06696 a.u. (red).

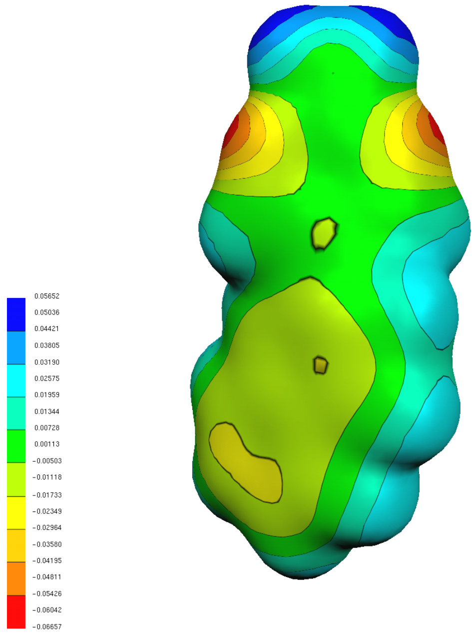

Figure 3: MEP of **6**, range: 0.05652 a.u.(blue) to -0.06657 a.u. (red).

Cartesian coordinates (in Å) of **4**:

6	1.885412	-1.147839	-0.374341
6	1.162777	0.000670	0.000381
6	1.887793	1.148067	0.373952
6	3.284370	1.148215	0.369013
6	3.988868	-0.001539	-0.001856
6	3.282018	-1.150169	-0.371622
6	-0.317085	0.001175	0.001326
6	-1.079581	1.105860	-0.413752
7	-2.411281	1.125561	-0.420211
6	-3.023119	-0.001150	-0.002820
7	-2.410662	-1.122805	0.427185
6	-1.079030	-1.101765	0.422252
7	-4.387596	-0.015519	-0.039919
1	1.354344	2.043230	0.694794
1	3.824669	2.047511	0.667090
1	5.079146	-0.002358	-0.002764
1	3.820430	-2.050278	-0.670644
1	1.349853	-2.041974	-0.694534
1	-0.585935	-2.004216	0.792375
1	-0.587123	2.012835	-0.773467
1	-4.871767	0.852549	-0.206554
1	-4.871375	-0.777113	0.409116

Cartesian coordinates (in Å) of **5**:

6	1.407167	-0.166354	-0.030802
6	0.332863	0.787362	0.058571
6	0.638866	2.135896	0.175378
6	1.976567	2.594395	0.230812
6	3.018770	1.695837	0.177594
6	2.763917	0.302999	0.043690
6	-1.092637	0.372192	0.029180
6	-2.006347	0.907050	-0.892549
7	-3.301469	0.593111	-0.918920
6	-3.714081	-0.294255	0.007353
7	-2.944500	-0.865887	0.956101
6	-1.656580	-0.525965	0.950383
7	-5.027716	-0.665933	-0.030641
1	-0.172940	2.859366	0.255644
1	2.173872	3.662083	0.330927
1	4.052267	2.039736	0.233923
1	-1.038573	-0.975647	1.731241
1	-1.667798	1.619603	-1.649122
1	-5.656128	-0.136336	-0.614357
1	-5.397568	-1.190302	0.746713
6	1.191185	-1.562073	-0.222983
6	2.247942	-2.445733	-0.304411
6	3.582842	-1.982121	-0.199554
6	3.830718	-0.636525	-0.034772
1	0.174598	-1.937055	-0.322418
1	2.055452	-3.508118	-0.456798
1	4.409912	-2.690065	-0.260679
1	4.855538	-0.268527	0.031794

Cartesian coordinates (in Å) of **6**:

6	3.093978	-1.644726	-0.292741
6	2.192263	-0.559173	-0.100790
6	0.782292	-0.733474	-0.132487
1	0.390792	-1.731337	-0.334955
6	2.728222	0.751766	0.121162
6	1.820121	1.831512	0.306109
6	0.458964	1.628368	0.275749
6	-0.091011	0.328404	0.054080
6	-1.556875	0.131708	0.028924
6	-2.442278	1.059822	-0.544750
7	-3.763552	0.896022	-0.583173
6	-4.236757	-0.240110	-0.032775
7	-3.498991	-1.199980	0.561186
6	-2.183106	-0.998027	0.582849
7	-5.584306	-0.447226	-0.100275
1	-0.212501	2.469252	0.448735
1	2.218996	2.830916	0.485761
6	4.139288	0.927108	0.149674
1	-1.589605	-1.765052	1.086710
1	-2.062181	1.972731	-1.009922
1	-6.172451	0.316889	-0.393517
1	-5.980573	-1.201953	0.437418
6	4.457983	-1.443247	-0.261156
6	4.986817	-0.145446	-0.036836
1	2.688554	-2.642772	-0.465234
1	5.137348	-2.283446	-0.408593
1	6.067214	0.000080	-0.013830
1	4.542945	1.926083	0.321193

Estimation of dipole-dipole and dipole-induced dipole interaction energies:

According to the central multipole expansion[2] the electrostatic energy (in SI units) $E_{\mu-\mu'}$ between two dipoles (with dipole moments μ and μ') is given by

$$E_{\mu-\mu'} = \frac{1}{4\pi\varepsilon_0}\frac{\mu\mu'}{2r^3}(2\cos\Theta\cos\Theta' + \sin\Theta\sin\Theta'\cos\xi)$$

(see reference [2(b)] for details).

The electrostatic energy (in SI units) E_{ind} between an induced dipole (α is the isotropic polarisability of the charge distribution, μ is the dipole moment) and a dipole is given by

$$E_{ind} = -\frac{\alpha}{4\pi\varepsilon_0}\mu^2\frac{1+3\cos^2\Theta}{(4\pi\varepsilon_0 r^3)^2}$$

(see reference [2(b)] for details).

The needed distances and angles were calculated as follows: First, the crystal coordinates were transformed into a Cartesian coordinate system. Then we centered in this global coordinate system *local* Cartesian coordinate systems at the center of mass of the individual molecules in the asymmetric unit. These local coordinate systems were rotated with respect to the global coordinate system, such that the nuclei positions with respect to the local coordinate system coincides with those of the coordinate system used in the DFT calculations, because the dipole vector components were known only in the latter. Now the distances and angles between the dipole moment vectors in the global coordinate system can be easily calculated. Because the crystal structures and the DFT equilibrium structures are not identical, this procedure is somewhat arbitrary, yielding only estimates for the electrostatic energies.

Aryl-aminopyrimidyl rotation barrier of 4:

Compound **4** shows the largest discrepancies for the aryl-aminopyrimidyl dihedral angle in solid state and gas phase (i.e., in the KS-DFT equilibrium structure). To get an estimate of the barrier for rotation about the aryl-aminopyrimidyl axis we performed for **4** a relaxed potential energy surface scan. We choose the semiempirical AM1[3] method to get a qualitative energy profile and for the height of the rotation barrier we optimized the saddle points on the B3LYP/aug-cc-pVDZ hypersurface (the method used for obtaining equilibrium structures). The subsequent normal mode analyses proved the obtained stationary points to be transition states (first order saddle points).

Figure 4 shows the AM1 energy profile, rescaled with the B3LYP barrier heights. The first saddle point, named **SP1**, (in Figure 4 located at $\tau+\tau_0=60°$) with a aryl-aminopyrimidyl dihedral angle of 90° is lower in energy than the second saddle point, named **SP2**, with a aryl-aminopyrimidyl dihedral angle of 180° (in Figure 4 located at $\tau+\tau_0=150°$).

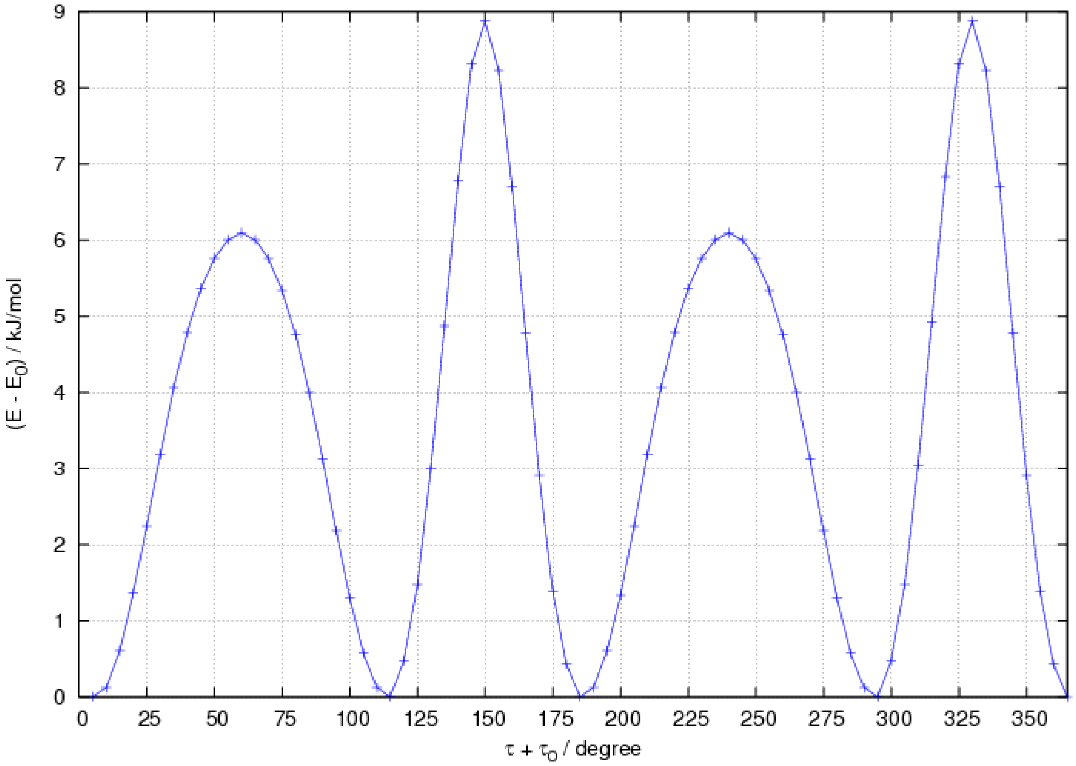

Figure S4: Energy profile for rotation about the aryl-aminopyrimidyl dihedral axis. τ_0 (E_0) is the equilibrium value of the aryl-aminopyrimidyl dihedral angle (the equilibrium energy), $\tau+\tau_0$ (E) is its actual value, τ is the actual displacement.

Electronic energies and Cartesian coordinates (in Å) of saddle points:

E_{el}(**SP1**) / a.u. = -550.820840,
E_{el}(**SP2)** / a.u. = -550.821900.

SP1:

6	1.209346	-1.884215	0.000000
6	0.000176	-1.169095	0.000000
6	-1.206595	-1.888234	0.000000
6	-1.204884	-3.286494	0.000000
6	0.004835	-3.987561	0.000000
6	1.212219	-3.282449	0.000000
1	-2.152659	-1.345694	0.000000
1	-2.151127	-3.828903	0.000000
1	0.006653	-5.077989	0.000000
1	2.160253	-3.821708	0.000000
1	2.153543	-1.338471	0.000000
6	-0.001800	0.321979	0.000000
6	-0.005626	1.078609	1.180405
6	-0.005626	1.078609	-1.180405
7	-0.005626	2.411925	1.201571
7	-0.005626	2.411925	-1.201571
6	0.001461	3.022877	0.000000
7	0.043915	4.388767	0.000000
1	-0.011562	0.580172	-2.153366
1	-0.011562	0.580172	2.153366
1	-0.121603	4.869971	0.870102
1	-0.121603	4.869971	-0.870102

SP2:

6	-0.002649	1.092792	1.176933
6	-0.000849	0.320169	0.000000
6	-0.002649	1.092792	-1.176933
7	0.000266	2.423910	-1.199207
6	0.007409	3.038298	0.000000
7	0.000266	2.423910	1.199207
6	-0.002266	-1.167119	0.000000
6	-0.002649	-1.902895	1.202845
6	-0.003814	-3.298734	1.203667
6	-0.004392	-4.009006	0.000000
6	-0.003814	-3.298734	-1.203667
6	-0.002649	-1.902895	-1.202845
7	0.045235	4.401535	0.000000
1	-0.001846	-1.390710	2.162804
1	-0.004085	-3.833865	2.153831
1	-0.005000	-5.099103	0.000000
1	-0.004085	-3.833865	-2.153831
1	-0.001846	-1.390710	-2.162804
1	-0.008923	0.618680	-2.159166
1	-0.008923	0.618680	2.159166
1	-0.087861	4.888702	0.871919
1	-0.087861	4.888702	-0.871919

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[1] G. Schaftenaar, J. H. Noordik, *J. Comput.-Aided Mol. Design*, 2000, 124-124.

[2] (a) A. D. Buckingham, *Quarterly Reviews of the Chemical Society*, 1959, **50**, 217-227. (b) Andrew R. Leach, *Molecular Modelling: Principles and Applications*, 2001, Prentice Hall, Harlow.

[3] Michael J. S. Dewar, Eve G. Zoebisch, Eamonn F. Healy, James J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902-3909.