Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for "Rubrene Untwisted: Common Density Functional Theory Calculations Overestimate Its Deviant Tendencies"

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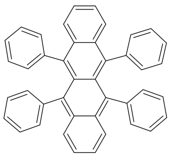
S1 Gas-phase twisting energies

Table S1 lists the root-mean-square errors for each method across the twisting potential energy scans corresponding to Figure 2 in the main paper. For comparison with earlier studies,[1,2] Table S2 supplements Table 1 from the main paper with twisting energies computed with three additional density functionals: ωB97, ωB97X-D, and M06-L. All three perform notably worse than SCS-MP2D relative to the DLPNO-CCSD(T) benchmarks.

Table S1: Root-mean-square errors for the rubrene derivative twisting potential energy scans relative to the benchmark DLPNO-CCSD(T) energies, in kJ/mol.

System	PBE-D3(BJ)	B86bPBE-XDM	B3LYP-D3(BJ)	MP2D	SCS-MP2D
Rubrene	2.67	2.85	2.33	0.53	0.22
F_{14}-Rubrene	3.70	4.20	3.38	0.23	0.23
Perfluororubrene	4.33	4.68	3.02	0.66	0.67
All three	**3.63**	**3.98**	**2.94**	**0.51**	**0.43**

Table S2: Predicted gas-phase twisting energies (kJ/mol) for rubrene and several derivatives as computed with three additional density functionals and the RMSE relative to the DLPNO-CCSD(T) benchmarks.



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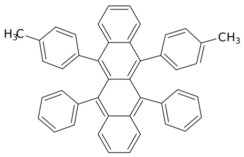

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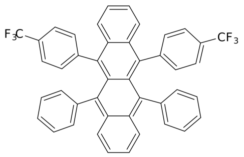

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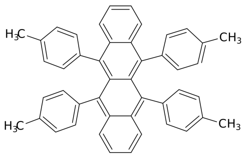

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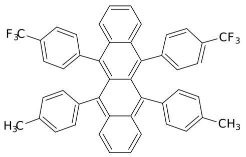

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Species	ωB97^a cc-pVDZ	ωB97X-D def2-QZVP	M06-L def2-QZVP	MP2D CBS	SCS-MP2D CBS	DLPNO-CCSD(T) CBS
1	-11.3	-10.5	-13.7	-8.6	-9.4	-9.3
2	-11.8	-10.4	-13.8	-8.4	-9.1	-9.0
3	-10.7	-10.8	-12.7	-7.8	-8.6	-9.0
4	-10.3	-9.4	-13.3	-7.7	-8.4	-8.4
5	-11.2	-8.7	-12.3	-6.8	-7.5	-7.2
RMSE	2.6	1.4	4.6	0.8	0.2	

[a] Ref 1

S2 Delocalization error

To characterize the delocalization error associated with rubrene twisting, Figure S1 plots two electronic properties of tetracene for the BLYP family of density functionals as a function of the exact exchange. Figure S1a examines the Mulliken charges (computed with the 6-31G(d) basis set) for the symmetrically unique carbon atoms. Similar to what was seen for the twisting energies (Figure 3) in the main paper, the charges vary nearly linearly with the increasing amount of exact exchange included in the functional. Figure S1b plots the change in the HOMO and LUMO orbital energies, which also exhibit the expected variation with increasing amounts of exact exchange.

Moreover, twisting tetracene has a negligible impact on these properties. The mean absolute atomic charge change is only 0.003 a.u. between the planar and twisted conformations. Similarly, twisting alters the HOMO and LUMO orbital energies by 0.03 eV or less. In other words, the twisting does not appear to impact the extent of π conjugation significantly.

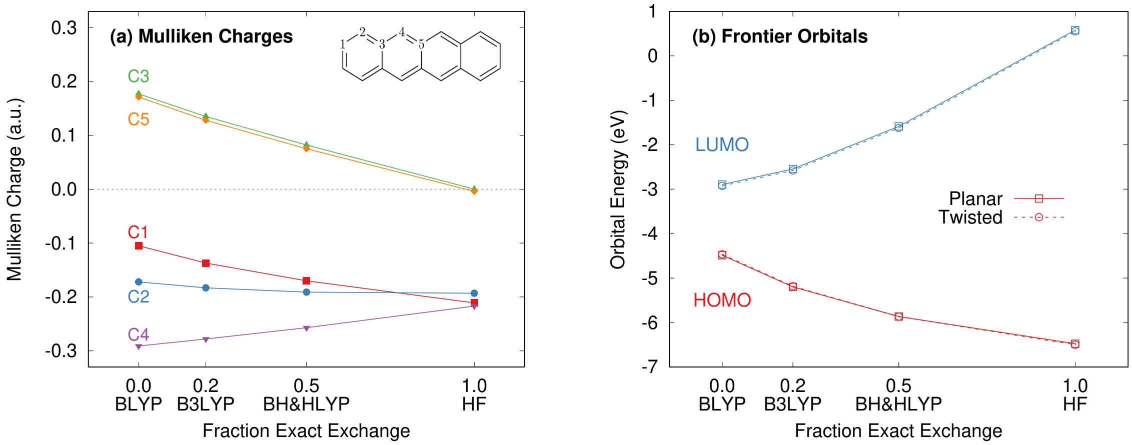

Figure S1: Impact of increasing the fraction of exact exchange in the functional on the (a) Mulliken charges for the carbon atoms and (b) frontier orbital energies for the tetracene backbone.

S3 Solid state polymorph energies

Table S3 lists the relative polymorph energies for perfluororubrene and rubrene before and after monomer correction. These energies match Figure 5 in the main paper. Table S4 summarizes the same energies, albeit using unit cells in which the lattice parameters were constrained at their experimental values (∼173–175 K) as the atomic positions were relaxed. Both sets of structure provide the same qualitative picture: the simpler GGA and hybrid DFT functionals substantially over-stabilize the twisted form of of perfluororubrene, and the polymorph stabilities are reversed upon performing the monomer correction with higher-level models like SCS-MP2D. In addition to the SCS-MP2D results presented in the main paper, these tables also show that dispersion-corrected MP2D with no spin-component-scaling gives qualitatively similar results. Table S5 lists the Monkhorst-Pack k-point grids used in the periodic DFT calculations.

Table S3: Relative polymorph energies for perfluororubrene and rubrene, in kJ/mol. The B86bPBE-XDM results were computed with periodic DFT, while the monomer-corrected values represent the B86bPBE-XDM results after correcting the monomer conformational energies with the indicated level of theory (as denoted with a Δ symbol).

Fully Optimized Unit Cells

	Perfluororubrene		Rubrene		
Method	Planar	Twisted	Orthorhombic	Monoclinic	Triclinic
Periodic DFT					
B86bPBE-XDM	0.0	-3.51	0.0	1.22	1.32
Monomer-corrected					
+ΔPBE-D3(BJ)	0.0	-3.30	0.0	2.24	2.13
+ΔB3LYP-D3(BJ)	0.0	-3.01	0.0	1.11	-0.08
+ΔωB97X-V	0.0	-0.32	0.0	1.17	-0.96
+ΔMP2D	0.0	4.41	0.0	0.83	0.17
+ΔSCS-MP2D	0.0	3.11	0.0	1.05	-0.28
+ΔDLPNO-CCSD(T)	0.0	4.46	0.0	1.98	-0.71

Table S4: Relative polymorph energies for Perfluororubrene and Rubrene, in kJ/mol, but using experimental lattice constants. The results change by less than 1 kJ/mol relative to Table S3.

Lattice Constants Constrained to ∼173–175K Experimental Values

	Perfluororubrene		Rubrene		
Method	Planar	Twisted	Orthorhombic	Monoclinic	Triclinic
Periodic DFT					
B86bPBE-XDM	0.0	-4.44	0.0		
Monomer-corrected					
+ΔPBE-D3(BJ)	0.0	-4.14	0.0	1.25	1.94
+ΔB3LYP-D3(BJ)	0.0	-3.56	0.0	0.04	-0.15
+ΔωB97X-V	0.0	-0.94	0.0	0.42	-0.86
+ΔMP2D	0.0	3.74	0.0	0.13	0.14
+ΔSCS-MP2D	0.0	2.60	0.0	0.20	-0.31

Table S5: Monkhorst-Pack k-point grids used for the periodic DFT calculations and root-mean-square deviations (rmsd15,[3] excluding hydrogen atoms) between the fully optimized and experimental crystal structures.

Polymorph	CSD RefCode	K-point grid	rmsd15 (Å)
	Perfluororubrene		
Planar	INELUK02	(3,3,1)	0.080
Twisted	INELUK03	(1,3,1)	0.087
	Rubrene		
Orthorhombic	QQCIG07	(1,5,1)	0.198
Monoclinic	QQCIG13	(3,3,1)	0.153
Triclinic	QQCIG14	(5,3,3)	0.151

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