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Supporting Information

A straightforward method to quantify the electron-delocalizing ability of π conjugated molecules

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Computational methods

Computational chemistry calculations were performed using Gaussian16/C.01.¹ Torsion scans were performed with steps of 10°. The D3 dispersion correction was used with all B3LYP geometry optimizations.² The Gaussian16 "external" feature was used to save a checkpoint file corresponding to the final geometry at each step of the torsion scan. If the Gaussian16 "external" feature is not available, then it is necessary to run a single-point calculation for each geometry-optimized scan step to generate a checkpoint file. The resulting checkpoint files were converted to formatted checkpoint (fchk) files.

Multiwfn³ was used to generate the LIDI matrix for each checkpoint file (in Multiwfn this functionality can be accessed through menu 15, then 4, then "y"). In Multiwfn we used fuzzy atomic space analysis with Becke partitioning. As noted in the main text, references to delocalization index (DI) in this work are, in all cases, to be interpreted as the delocalization index calculated in fuzzy atomic space. The delocalization index matrix files were then processed using a Python script to determine the IFDI values. The Python script sums the delocalization indices between atoms on different fragments, where the fragments are defined, using atom numbers, by user input. The Python script is available on Github (https://github.com/martinp23/ifdi) or via Zenodo (https://doi.org/10.5281/zenodo.6471792).

Molecular orbital isosurfaces were plotted using Chimera.

Supplementary figures



Figure S1: Key to compounds and symbols used elsewhere in the ESI document. For example, diphenyldiacetylene is BYYB, while a diacetylene-linked *meso*-porphyrin dimer is PmYYPm.



Figure S2: Effect of torsion barrier on population of conformers; (a) shows that with increasing torsion barrier, the population of near-planar conformers increases; (b) shows that with increasing torsion barrier, a greater fraction of molecules (f) have a torsion angle between 0 and 60°.



Figure S3: Change in delocalization index as a function of torsion angle for diphenyldiacetylene, $DI_q - DI_0$, where DI_q is the matrix of delocalization indices for the conformer with torsion angle *q*. Blue is positive; red is negative; the same scale is used on all subplots. Level of theory: B3LYP/6-31G*.



Figure S4: Effect of choice of computational method on IFDI as a function of torsion angle for diphenyldiacetylene. All calculations used the 6-31G* basis set.



Figure S5: Effect of choice of computational method on Δ IFDI and torsion barrier for diphenyldiacetylene. All calculations used the 6-31G* basis set.



Figure S6: Comparison of IFDI as a function of torsion angle for butadiyne-linked: (a) norcorrole dimers, linked through the β position (shown as Nb in SI Figure S1); (b) porphyrin dimers, linked through the *meso* position (shown as Pm in SI Figure S1). Level of theory: B3LYP/6-31G*.



Figure S7: Comparison of delocalization parameters as a function of torsion angle for benzene dimers with different linkers (see legend). (a) shows the IFDI calculated as the sum of DIs between atoms on different benzene fragments; (b) shows only the DI between the carbon atoms *para* to the linker. Level of theory: B3LYP/6-31G*.



Figure S8: Comparison of IFDI as a function of torsion angle for indacene dimers connected through the 1- and 2-positions (see main text Figure 1 for numbering scheme). Level of theory: B3LYP/6-31G*.



Figure S9: Highest (H) occupied molecular orbital and lowest (L) unoccupied molecular orbital of indacene. Level of theory: B3LYP/6-31G*.



Figure S10: IFDI as a function of torsion angle for directly-linked dimers of benzene, pyrrole, fluorene, and thiophene. Level of theory: B3LYP/6-31G*. The IFDI is shown (a) excluding and (b) including the H atoms of the dimers.



Figure S11: IFDI as a function of torsion angle for model molecular wires (general structure depicted in Figure 5) with different bridges. The molecular wires have the structure (a) BY{X}YB and (b) BYY{X}YB, where {X} is the bridging group indicated in the figure legend. Level of theory: B3LYP/6-31G*.



Figure S12: IFDI as a function of torsion angle for model molecular wires with alkyne-substituted bridges (calculated with the BY {X}YB model, as above), similar to those reported by Breslow and co-workers.⁴ Level of theory: $B3LYP/6-31G^*$.



Figure S13: IFDI as a function of torsion angle for alkyne-linked molecular wires of the form BY{X}YB, where {X} is the norcorrole or porphyrin bridge unit shown in the figure legend. Level of theory: $B3LYP/6-31G^*$.



Figure S14: (a) A schematic for the molecular wire model, with the 4 and 4' carbon atoms highlighted; (b) Correlation between $\Delta DI_{4,4'}$ and the $b_{X,expt}$ value for single-molecule conductance, $b_{X,expt}$ values are from ref 3, and DI values were calculated using B3LYP/6-31G*. The *meta*-phenylene linker has a larger $b_{X,expt}$ than predicted by DI, possibly owing to a σ -delocalization effect, and is excluded from the fit line.



Figure S15: Correlation between Δ IFDI and the $b_{X,expt}$ value for single-molecule conductance, $b_{X,expt}$ values are from ref 4. The *meta*-phenylene linker has a larger $b_{X,expt}$ than predicted by IFDI, possibly owing to a s-delocalization effect, and is excluded from the fit line. The datapoint for *m*-phenylene ($b_{X,expt} \sim -2.75$) is absent for ω B97XD, because its Δ IFDI is negative and near zero.

Supplementary tables

Compound	Level of theory	ΔIFDI (x10-2)	ΔE_{0-90° (kJ/mol)
BYYB	B3LYP	1.12	1.14
BYYB	PBE//B3LYP	1.58	1.45
BYYB	ωB97XD//B3LYP	0.53	0.44
BYYB	PBE	1.80	1.48
BYYB	B3LYP//PBE	1.29	1.14
BYYB	$\omega B97 XD//PBE$	0.61	0.43
BYYB	ωB97XD	0.45	0.52
BYYB	PBE//@B97XD	1.37	1.30
BYYB	B3LYP//ωB97XD	0.96	1.07
BYYB	BLYP	1.79	1.48
BYYB	B1LYP	0.99	1.04
BYYB	LC-whPBE	0.28	0.37
BYYB	M06-2X	0.55	0.64
BYYB	HF	0.23	0.22
PmYYPm	PBE	6.39	3.41
PmYYPm	B3LYP	3.80	2.48
PmYYPm	ωB97XD	1.33	0.16
PmYYPm	LC-whPBE	0.86	-0.36
PmYYPm	CAM-B3LYP	1.66	0.79
PmYPm	B3LYP	19.7	1.01 <i>ª</i>
NbYYNb	PBE	53.3	15.8
NbYYNb	B3LYP	7.26	4.54
NbYYNb	ωB97XD	1.24	0.85
NbYYNb	LC-whPBE	0.64	0.25
NbYYNb	CAM-B3LYP	1.67	1.41
PbYYPb	B3LYP	2.08	1.31
NmYYNm	B3LYP	4.70	3.11
I1YYI1	B3LYP	14.2	9.86
I2YYI2	B3LYP	2.83	1.91
BP5YYBP5	B3LYP	4.36	3.55
BP2YYBP2	B3LYP	1.94	1.79
BYYYB	B3LYP	0.55	0.41
BYYYYB	B3LYP	0.29	0.16
FYYF	B3LYP	1.58	1.52
pushBYYBpull ^b	B3LYP	2.17	2.87

Table S1: Δ IFDI and Δ E_{0-90°} for various dimers defined using the terminology in Fig. S1. All calculations used the 6-31G* basis set.

<u>pushBYYBpull</u>^{*b*} B3LYP 2.17 2.87 ^{*a*} the torsion angle of the minimum energy conformer of PmYPm is ~30°, which is ~8.1 kJ/mol lower in energy than the 90° conformer; ^{*b*} in pushBYYBpull, one phenyl ring bears a *para* nitro (NO₂), and the other a *para* amine (NH₂) (4-((4-nitrophenyl)buta-1,3-diyn-1-yl)aniline).

Table S2: Δ IFDI for various for alkyne-linked molecular wires of the form BY{X}YB or BYY{X}YB. All calculations used the B3LYP/6-31G* level of theory. The Δ IFDI refers to the IFDI between the terminal phenyl rings in the molecular wire models.

{X} in wire	Linker	∆IFDI with H	∆IFDI without	∆E (kJ/mol)
		atoms	H atoms	
1,4-phenylene	Y	2.53×10^{-3}	2.47×10^{-3}	4.56
furan	Υ	3.64×10^{-3}	3.55×10^{-3}	4.95
thiophene	Υ	3.45×10^{-3}	3.37×10^{-3}	4.71
cyclopentadiene	Υ	4.20×10^{-3}	4.10×10^{-3}	6.30
cyclopentadienone	Υ	4.29×10^{-3}	4.18×10^{-3}	7.63
1,3-phenylene	Υ	2.18×10^{-6}	2.65×10^{-6}	3.82
Nm	Υ	1.25×10^{-3}	1.22×10^{-3}	7.19
Pm ^a	Υ	9.98×10^{-4}	9.72×10^{-4}	5.06
Nb	Υ	3.21×10^{-5}	3.14×10^{-5}	5.79
Pb ^a	Υ	1.19×10^{-4}	1.16×10^{-4}	4.26
1,4-phenylene	YY	6.59×10^{-4}	6.43×10^{-4}	1.48
furan	YY	9.83×10^{-4}	9.59×10^{-4}	1.39
thiophene	YY	9.51×10^{-4}	9.28×10^{-4}	1.46
cyclopentadiene	YY	1.19×10^{-3}	1.16×10^{-3}	2.13
cyclopentadienone	YY	1.34×10^{-3}	1.31×10^{-3}	2.81

^a A nickel(II) porphyrin model was used, for direct comparability with the norcorroles Nm and Nb.

References

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Cartesian coordinates

Cartesian coordinates for planar geometries are provided in XYZ files as supplementary information.