Supporting information section

Quinonoid vs. aromatic structures of heteroconjugated polymers from oligomer calculations

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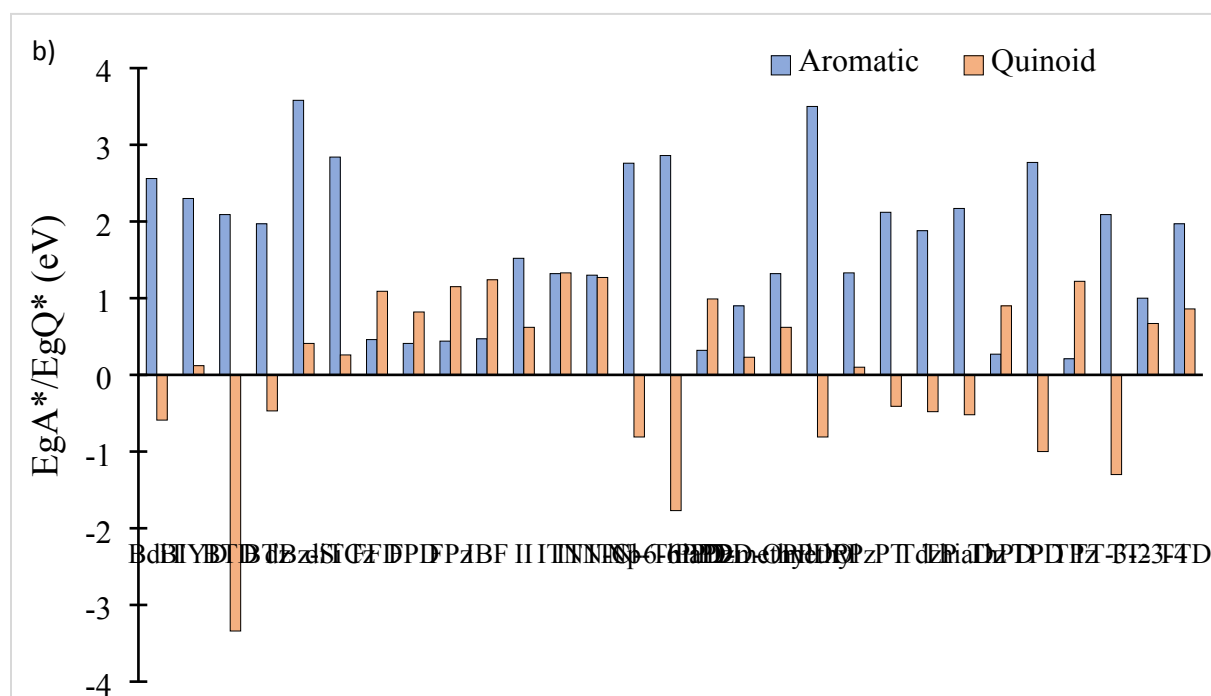**Fig. S1** Band gaps of heteroconjugated polymers for their optimized aromatic structures, Eg_A, (blue) and their respective quinonoid structures, Eg_Q, (orange). Values were obtained by a) linear extrapolation and b) quadratic extrapolation from calculation of different n-mers optimized by PBE0/6-31G(d). The unphysical negative gaps are discussed in the text. The repeat units are illustrated in Scheme 3.
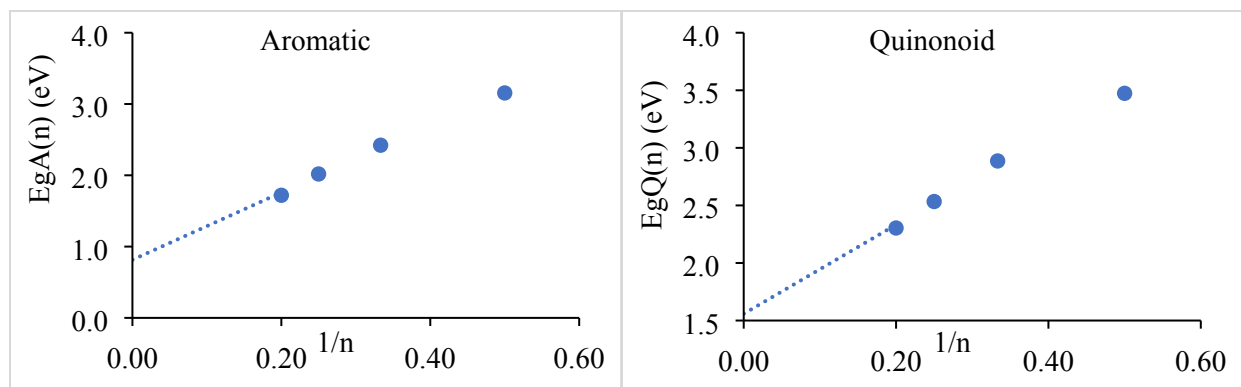
Fig. S2 Band gaps of n-mers ($Eg_A(n)/Eg_Q(n)$) as a function of 1/n for aromatic and quinonoid structures of the IBF polymer.

The linear extrapolation is illustrated in Figure S2 for the IBF polymer, where the linear extrapolated band gap in the aromatic form is 0.81 eV while in quinonoid form the band gap is extrapolated to 1.56 eV. The band gaps of the IBF oligomers are obtained using eq 4 and 5 (shown in the main text) and are tabulated in Table S1.
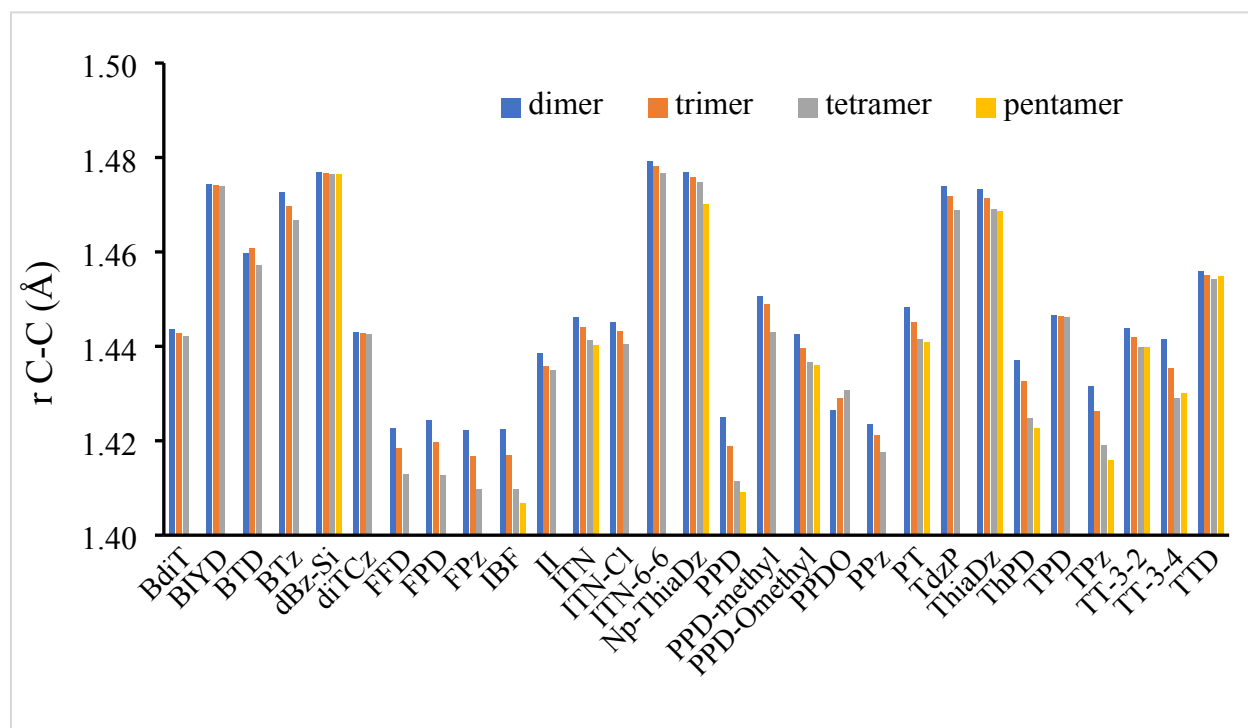
Fig. S3 Plot of distance between two adjacent heterocyclic units at the center of the oligomer, r_{C-C} (Å), in the optimized aromatic structures with different oligomer units as calculated by PBE0/6-31G(d).

Fig. S4 Plot of CC bond distance between two adjacent heterocyclic rings at the center of the chain, r_{C-C} (Å), in the optimized quinonoid structure of heteroconjugated polymers with different oligomer units calculated by DFT method PBE0/6-31G(d).
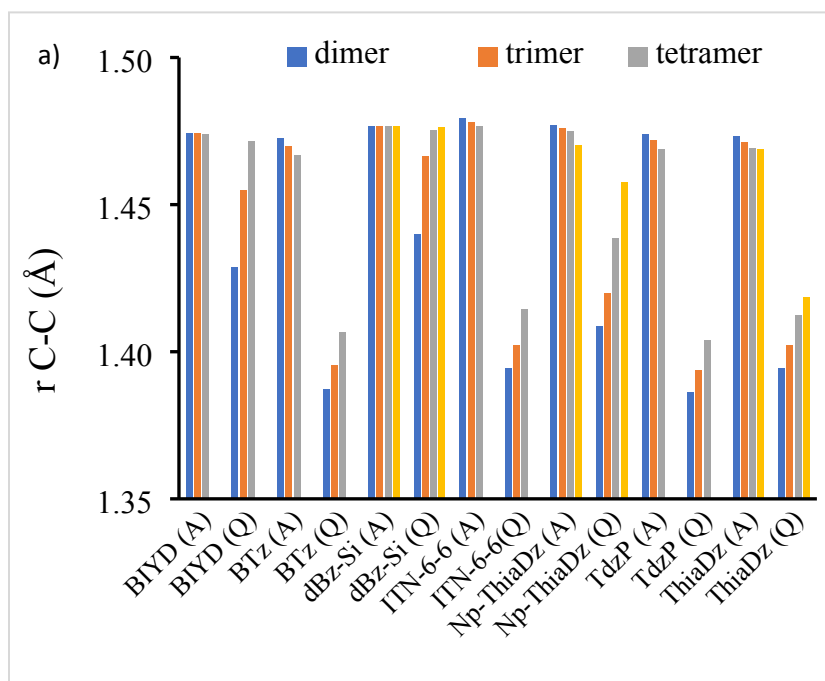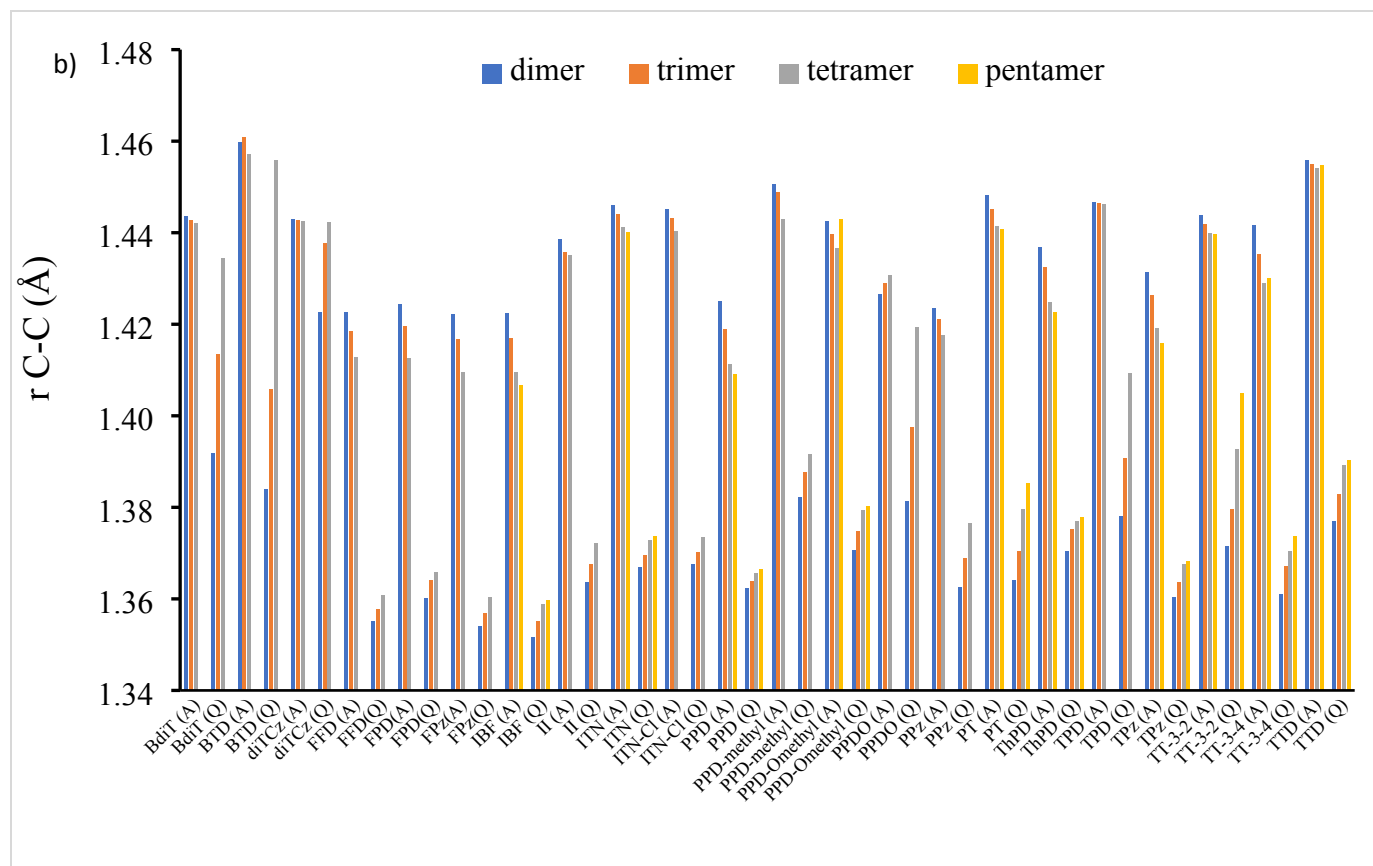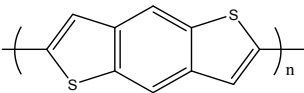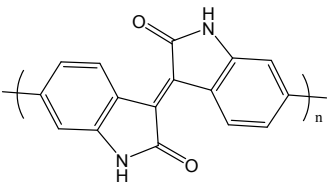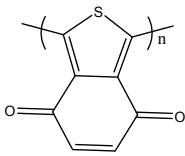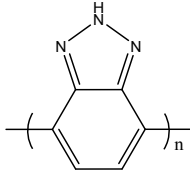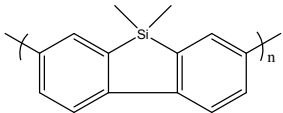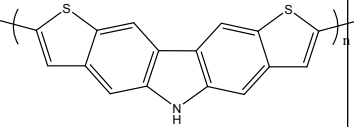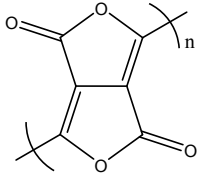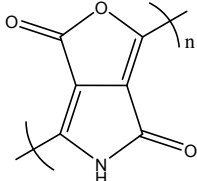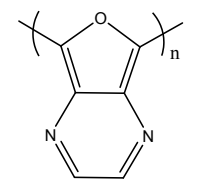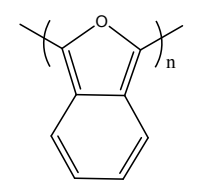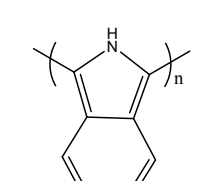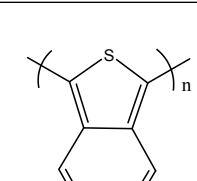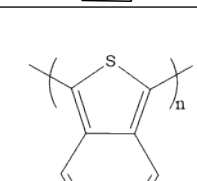
Fig. S5 Plot of CC bond distances, r_{C-C}, between two adjacent central repeat units in the polymer. a) 6-membered ring to 6-membered link, and b) 5- membered ring to 5-membered link, in heteroconjugated polymers with different oligomer units for their aromatic (A) and quinonoid (Q) structures calculated by PBE0/6-31G(d).

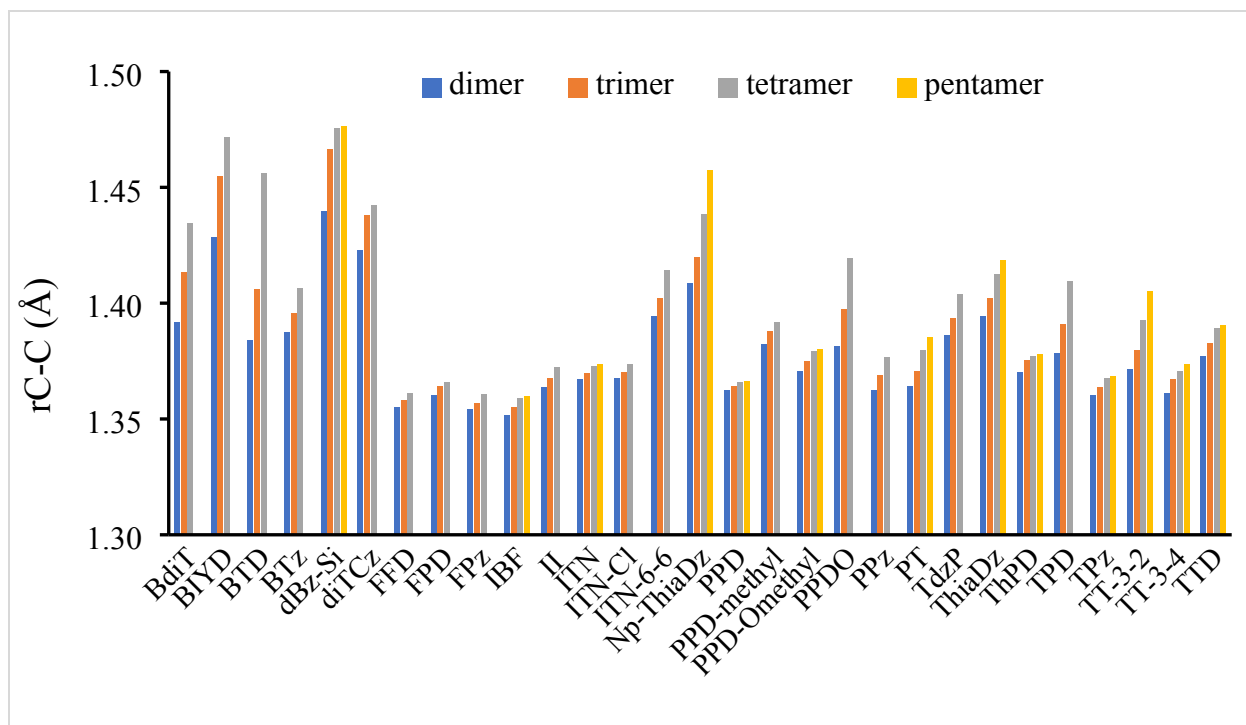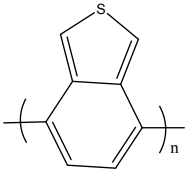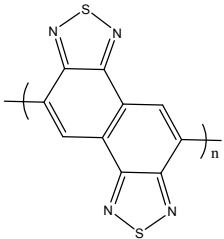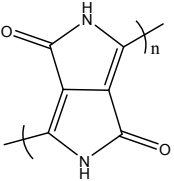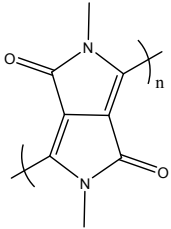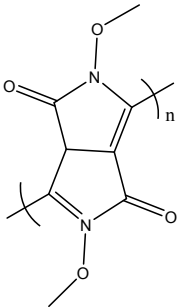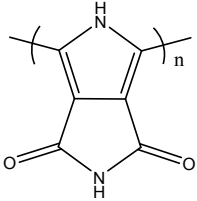**Table S1** Calculated band gaps of n-mers ($Eg_A(n)/Eg_Q(n)$) for aromatic and quinonoid structures of the IBF polymer with PBE0/6-31G(d)
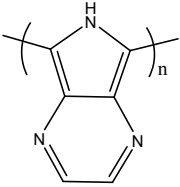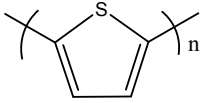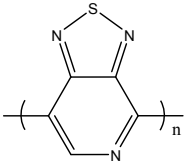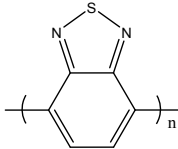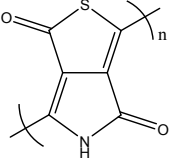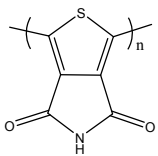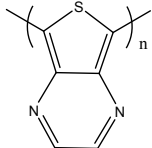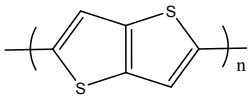
n	1/n	aromatic			quinonoid		
		$E_A^{(HOMO)}(n)$ (eV)	$E_A^{(LUMO)}(n)$ (eV)	$Eg_A(n)$ (eV)	$E_Q^{(HOMO)}(n)$ (eV)	$E_Q^{(LUMO)}(n)$ (eV)	$Eg_Q(n)$ (eV)
2	0.50	-4.747	-1.592	3.155	-0.185	-0.057	0.128
3	0.33	-4.387	-1.965	2.422	-0.173	-0.067	0.106
4	0.25	-4.195	-2.176	2.018	-0.166	-0.072	0.093
5	0.20	-4.055	-2.336	1.720	-0.161	-0.076	0.085
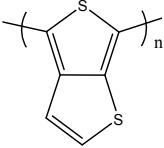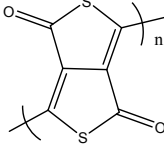
Table S2 Names and structures of the polymers under study listed with the sizes of longest n-mer used for calculations.

Abbreviation	Name	structure	Size, the n value, of the *longest* oligomer for which computed data are used
BdiT	poly(benzo-1,2-b:4,5-b'-dithiophene)		4
BIYD	poly(E-3,3'-biindolinylidene-2,2'-dione)		4 (Note that the repeat unit in this case consists of two chemical repeat units)
BTD	poly(benzo[c]thiophene-4,7-dione)		4
BTz	poly(2H-benzo-1,2,3-triazole)		4
dBz-Si	poly(5,5-dimethyldibenzosilole)		5
diTCz	poly(dithieno-3,2-b:2',3'-h-carbazole)		4

FFD	Poly(furo[3,4-c]furan-1,4-dione)		4
FPD	Poly(furo[3,4-c]pyrrole-1,4-dione)		4
FPz	poly(furo[3,4-b]pyrazine)		4
IBF	poly(isobenzofuran)		5
II	poly(2H-isoindole)		4
ITN	poly(benzo[c]thiophene)		5
ITN-Cl	poly(5,6-dichlorobenzo[c]thiophene)		4

ITN-6-6	poly([6-6]benzo[c]thiophene)		4
Np-thiaDz	poly(naphtho-1,2-c:5,6-c'-bis-1,2,5-thiadiazole)		5
PPD	poly(2,5-dihydropyrrolo-3,4-[c]pyrrole-1,4-dione)		5
PPD-methyl	poly(2,5-dimethyl-2,5-dihydropyrrolo-3,4-[c]pyrrole-1,4-dione)		4
PPD-Omethyl	poly(2,5-dimethoxy-2,5-dihydropyrrolo-3,4-[c]pyrrole-1,4-dione)		5
PPDO	poly(pyrrolo-3,4-[c]pyrrole-1,3-dione)		4

PPz	poly(6H-pyrrolo[3,4-b]pyrazine)		4
PT	poly(thiophene)		5
TdzP	poly(1,2,5-thiadiazolo-3,4-[c]pyridine)		4
Thia-Dz	poly(benzo-1,2,5-thiadiazole)		5
ThPD	Poly(thieno[3,4-c]pyrrole-1,4-dione)		5
TPD	poly(thieno-3,4-[c]pyrrole-4,6-dione)		4
TPz	poly(thieno-3,4-[b]pyrazine)		5
TT-3-2	poly(thieno-3,2-[b]thiophene)		5

TT-3-4	poly(thieno-3,4-[b]thiophene)		5
TTD	Poly(thieno[3,4-c]thiophene-1,4-dione)		5

Method validation

We have applied DFT methods combined with a simple extrapolation procedure in order to obtains insights into the specific aspect of conjugated polymers, namely their preferences of aromatic vs. quinonoid structures. While we obtained consistent data using the PBE0/6-31G(d) functional and basis set combination, we present below background information regarding this choice.

a) Choice of DFT

It is widely reported that B3LYP combined with a basis set of the quality of 6-31G(d) or higher produces reasonable bandgaps for organic conjugated polymers.[1,2] The exact exchange content of B3LYP is A_x=0.20. The bandgaps produced by B3LYP are about 20% underestimated. It has been demonstrated that methods with A_x=0.25 improve the agreement with experimental bandgaps.[3] This is behind our choice of the PBE0[4] density functional which incorporates an exchange with A_x=0.25. The improvement is largely due to the increased exact exchange content based on the strong correlation between A_x and the bandgap.[1] The best agreement for the three conjugated polymers discussed in reference [3] is found to be with the use of PBE0 out of a group of seven density functionals plus Hartree-Fock. Among various DFT methods used by Yang, the r_{c-c} and band gap values for the PBE0 agreed very well with the experiment values. Our choice has been based on these findings and validation.

Bond length alternation (BLA) values are critically important in this study because of the comparison of aromatic vs. quinonoid structures. Optimized BLA values also strongly support an A_x value close to 0.2-0.25.[3] In this respect both B3LYP and PBE0 perform very well.[3, 5] However, wB97X with A_x=0.22 produces BLA values that are 40% too large.[5] Another popular DFT, M06-2X (A_x=0.54), also gives a BLA value that are too large and also gives bandgap values that are too large.

Further, we performed additional calculations to validate our work. We performed calculations on systems such as TPz, TTD and ThiaDz using M06-2X/6-31G(d). The difference between r_{c-c} distance calculated using PBE0/6-31G(d) and M06-2X/6-31G(d) obtained shown in Table S3 ranging from 0.01 to 0.014 $\overset{\circ}{A}$ (larger with M06-2X functional). As discussed above, the band gap values obtained are larger with M06-2X functional (variation of ~1.5 eV from PBE0). Table S4 shows the energy difference (ΔE), r_{c-c} and bandgap calculated using PBE0/6-31G(d) and wB97X/6-31G(d). The band gap values are overly estimated using wB97X. There is a small variation in the r_{c-c} distance ranging from 0.015 to 0.025 $\overset{\circ}{A}$ (larger with wB97X functional).

Table S3 Comparison of energy difference (ΔE(n)), r_{C-C} and bandgap of TPz, TTD and ThiaDz n-mers calculated using PBE0/6-31G(d) and M06-2X/6-31G(d) functionals and basis set.

n-mer		PBE0			M06-2X		
		Energy a.u.	r_{C-C} Å	bandgap eV	Energy a.u.	r_{C-C} Å	bandgap eV
TPz							
A	4	-2949.1655	1.419	1.79	-2950.6359	1.432	3.24
	5	-3686.1665	1.416	1.50	-3688.0041	1.430	2.90
Q	4	-3026.4925	1.368	2.26	-3028.0279	1.358	3.80
	5	-3763.4971	1.368	2.07	-3765.4018	1.358	3.59
ΔE(5) (kcal/mol)		-2.34			-3.54		
TTD							
A	4	-4700.1490	1.454	2.48	-4702.1562	1.461	4.24
	5	-5874.8900	1.455	2.38	-5877.4001	1.462	4.15
Q	4	-4777.4601	1.389	1.88	-4779.5302	1.365	3.64
	5	-5952.2004	1.390	1.69	-5954.7742	1.365	3.47
ΔE(5) (kcal/mol)		0.50			-0.05		
ThiaDz							
A	4	-2949.1679	1.469	3.07	-2950.6427	1.474	4.78
	5	-3686.1653	1.469	2.91	-3688.0098	1.474	4.60
Q	4	-3026.4250	1.412	1.60	-3027.9512	1.391	3.11
	5	-3763.4135	1.418	1.23	-3765.3048	1.394	2.70
ΔE(5) (kcal/mol)		5.63			8.47		

Table S4 Comparison of energy difference (ΔE(n)), r_{C-C} and bandgap calculated for TPz n-mers using PBE0/6-31G(d) and wB97X /6-31G(d) functionals and basis set.

n-mers		PBE0 Energy a.u.	r_{C-C} Å	bandgap eV	wB97X Energy a.u.	r_{C-C} Å	bandgap eV
A	4	-2949.1655	1.419	1.79	-2950.8505	1.444	5.24
	5	-3686.1665	1.416	1.50	-3688.2695	1.443	4.89
Q	4	-3026.4925	1.368	2.26	-3028.2607	1.353	5.89
	5	-3763.4971	1.368	2.07	-3765.6869	1.353	5.69
ΔE(5) (kcal/mol)		-2.34			-4.50		

b) The effect of an empirical dispersion term in DFT

We performed additional calculations, to include dispersion interactions, on TPz tetramer and pentamer over aromatic and quinonoid forms using PBE0/6-31G(d)+GD3BJ[6]. We observed only a very small difference in energy, the central r_{C-C} distance, and the bandgap (Table S5). Thus, the inclusion of the dispersion interaction is not necessary for our studies.

Table S5 Comparison of energy difference (ΔE(n)), r_{C-C} and bandgap of TPz n-mers calculated using PBE0/6-31G(d) and PBE0/6-31G(d)+GD3BJ[6] functionals and basis set.

n-mers		PBE0 Energy a.u.	r_{C-C} Å	bandgap eV	PBE0 with GD3BJ Energy a.u.	r_{C-C} Å	bandgap eV
A	4	-2949.1655	1.419	1.79	-2949.2408	1.417	1.77
	5	-3686.1665	1.416	1.50	-3686.2623	1.414	1.48
Q	4	-3026.4925	1.368	2.26	-3026.5740	1.366	2.27
	5	-3763.4971	1.368	2.07	-3763.5994	1.367	2.08
ΔE (kcal/mol)		-2.34			-2.46		

c) The effect of basis set

We performed calculations on aromatic TPz tetramer with PBE0 functional and various basis sets. On changing the basis set, very small difference in energy, r_{C-C} distance and bandgap were observed (Table S6). We performed calculations on TPz tetramer and pentamer both in aromatic and quinonoid form with PBE0/6-311+G(d,p) to compare with our initial calculations performed using PBE0/6-31G(d) (Table S7). Apart from negligible differences in r_{C-C} distance and bandgap, the ΔE value has a difference of only 0.02 kcal/mol. Thus, the size of basis set does not affect the overall results.

Table S6 Comparison of energy, r_{C-C} and bandgap of the aromatic structure of the TPz tetramer calculated using PBE0 functional and different basis sets.

	6-31G(d)	6-311G(d)	6-311G(d,p)	6-31+G(d,p)	6-311+G(d,p)
Energy (a.u.)	-2949.1655	-2949.5122	-2949.52863	-2949.2138	-2949.55251
r_{C-C} (Å)	1.419	1.419	1.418	1.421	1.419
gap (eV)	1.79	1.81	1.80	1.77	1.78

Table S7 Comparison of energy difference (ΔE(n)), r_{C-C} and bandgap of TPz n-mers calculated using PBE0/6-31G(d) and PBE0/6-311+G(d,p) functional and basis sets.

n-mer		PBE0/6-31G(d)			PBE0/6-311+G(d,p)		
		Energy a.u.	r_{C-C} Å	gap eV	Energy a.u.	r_{C-C} Å	gap eV
A	4	-2949.1655	1.419	1.79	-2949.5525	1.419	1.78
	5	-3686.1665	1.416	1.50	-3686.6481	1.416	1.50
Q	4	-3026.4925	1.368	2.26	-3026.8963	1.367	2.23
	5	-3763.4971	1.368	2.07	-3763.9955	1.367	2.04
ΔE (kcal/mol)		-2.34			-2.26		

This study includes two categories of extrapolation.

a) Extrapolation of the relative energies of the aromatic vs. quinonoid structures.

We follow the approach from reference [7]. The convergence properties of this approach are excellent for the systems under study here. An example is given below Table S8.

Table S8 Energy difference of n-mers of PPD both in aromatic and quinonoid form.

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n	$E_A(n)$ (a.u.)	$E_Q(n)$ (a.u.)	$\Delta E(n)$ (kcal/mol)
3	-489.2983	-489.3015	-2.01
4	-489.2987	-489.3015	-1.73
5	-489.2989	-489.3014	-1.58

Using equation (3), (4) and (5) in main text,

we calculated:

$E_A(5) = E_A^{(5)} - E_A^{(4)} =$ -2447.6389- (-1958.34)

$\qquad$ = -489.2989 a.u.

$E_Q(5) = E_Q^{(5)} - E_Q^{(4)} =$ -2524.9693- (-2035.6679)

$\qquad$ = -489.301409 a.u.

$\Delta E(5) = E_Q(5) - E_A(5) =$ -489.3014 - (-489.2989)

$\qquad$ = -0.0025 a.u.

$\qquad$ = -1.58 kcal/mol

The largest calculated n value for PPD is 5. $E_A(5)$ and $E_Q(5)$ was obtained from the difference of the optimized energy of the PPD pentamer and tetramer in aromatic and quinonoid form. $\Delta E(5)$ for PPD calculated from the difference of $E_A(5)$ and $E_Q(5)$ is also plotted in Fig. 1. Similarly, $\Delta E(4)$ and $\Delta E(3)$ were calculated shown in Table S8. The negative ΔE values indicate a quinonoid ground state preference of PPD. With increasing n, the energy difference between quinonoid form and aromatic form decreases but the values look converged and system still shows the preference for quinonoid ground state.

$\qquad$ b) Extrapolation of energy gaps.
A relatively large literature exists addressing extrapolation of energy gaps based on oligomer calculations.[2,8,9, 10,11,12,13,14,15] A comprehensive study comparing more than a dozen extrapolation schemes has been provided.[9] While the linear in 1/n extrapolations are not the best, they typically produce a fit with $R^2>0.9993$. The errors involved in the extrapolation are smaller than the errors due to the choice of the underlying quantum mechanical method, the choice of the density functional or the basis set.

$\qquad$ A $\qquad\qquad\qquad$ Q $\qquad\qquad\qquad$ Q
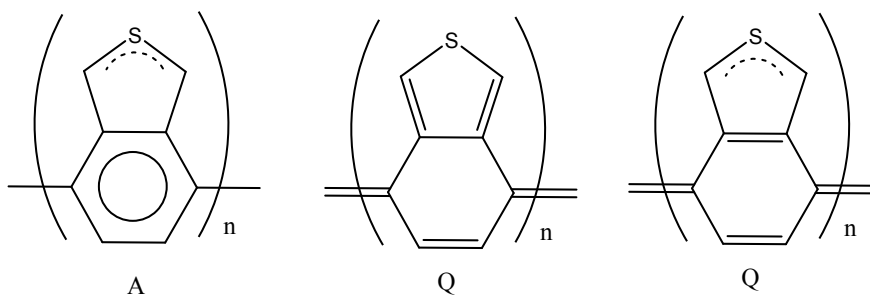
Scheme S1 Aromatic and quinonoid forms of one of the 6-6 connected conjugated polymers, ITN-6-6.

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