

Supporting Information

Regio(ir)regular Naphthalenediimide- and Perylenediimide-Bithiophene Copolymers: How MO Localization Controls the Bandgap

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Time-dependent (TD) calculations with a set of different functionals, i.e. (CAM)B3LYP, offset-corrected (OC-)M06HF^[A] (with an OC = 0.75 eV; for detailed see Ref. [B]), however not only considering the energy of the lowest singlet state (S_1), but the relevant S_n manifold in the visible range to verify whether the calculations are able to reproduce the experimental absorption spectra. For this, geometries of the co-oligomers (**NDI-2T**)_n and (**PDI-2T**)_n ($n = 1, 2, 3$) in the electronic (singlet) ground state (S_0) were optimized without symmetry restrictions at the B3LYP level of theory as defined in the Gaussian09 program package.^[C] Truncation to $n = 3$ was set by the limitations of the computational resources; absence of imaginary frequencies indicated true minima. Adiabatic energies of the first excited singlet state S_1 were obtained as energy differences of the optimized S_1 states using the respective TD functionals and the corresponding single point energies of the TD functionals at the B3LYP ground state geometries. The 6-311G* basis set was used for all calculations. For singlet-triplet gaps (*vide infra*), we relied on B3LYP calculations, which - different to CAM-B3LYP and M06HF - was shown to tackle this issue in a satisfactory way for DA systems.

Transition densities were calculated from the CI coefficients and ground state orbitals using Multiwfn v. 3.3.6.^[D] Natural transition orbital analysis (NTO) and transition densities were plotted in Gaussview (isosurface value 0.03). Gaussview was also used to plot the calculated absorption spectra in molar extinction coefficients ϵ_m ($M^{-1}\cdot cm^{-1}$), obtained from the calculated oscillator strength via $f = 4.319 \cdot 10^{-9} \int \epsilon_m(\nu) d\nu$ with $[\nu] = cm^{-1}$.

Extrapolation to the polymer limit was done with an exponential function $y = e^{-a \cdot N} + b$ (where N is the number of double bonds along the shortest path between the terminal C-atoms) as introduced by Meier.^[E]

1. M06HF results

Table S1a: Vertical $S_0 \rightarrow S_1$ electronic transition energies E with oscillator strength f , configuration interaction description (CI; only contributions $\geq 5\%$) of r/i -(**NDI-2T**) $_n$ oligomers calculated at the TD-DFT (M06HF//B3LYP(6-311G*)) level of theory.

System	state	E / eV (λ / nm)	f	main CI configuration
(NDI2T) ₁	S ₁	3.41 (364)	0.321	H→L (62%) H-4→L (9%) H→L+1 (7%) H-1→L (6%)
<i>r</i> -(NDI2T) ₂	S ₁	3.22 (386)	1.070	H→L (61%)
<i>i</i> -(NDI2T) ₂	S ₁	3.29 (377)	1.125	H→L (55%) H-1→L+1 (6%) H-1→L+2 (6%) H-8→L+1 (5%)
<i>r</i> -(NDI2T) ₃	S ₁	3.14 (395)	2.019	H→L (45%) H-1→L+1 (14%)
<i>i</i> -(NDI2T) ₃	S ₁	3.23 (383)	2.036	H→L (42%) H-1→L+1 (12%) H-2→L+3 (6%)

Table S1b: Vertical $S_0 \rightarrow S_n$ electronic transition energies E with oscillator strength f for such transitions with $f > 0.2 f_{\text{max}}$, CI description (contributions $\geq 5\%$) of r/i -(**PDI-2T**) $_n$ oligomers calculated at the TD-DFT (M06HF//B3LYP(6-311G*)) level of theory.

System	state	E / eV (λ / nm)	f	main CI configuration
(PDI2T) ₁	S ₁	3.02 (410)	0.889	H-1→L (62%) H→L (34%)
	S ₂	3.58 (346)	0.215	H→L (32%) H-1→L (17%) H-4→L (11%) H→L+1 (10%)
<i>r</i> -(PDI2T) ₂	S ₁	3.00 (413)	0.827	H-2→L+1 (37%) H-3→L (37%) H→L (10%) H-1→L (6%)
	S ₁ '	3.03 (409)	1.049	H-2→L+1 (33%) H-3→L (20%) H-2→L (12%) H→L+1 (11%) H-3→L+1 (8%) H-1→L (8%)
	S ₂	3.54 (351)	0.494	H→L (22%) H→L+1 (13%) H→L+2 (10%) H-8→L+1 (7%)
<i>i</i> -(PDI2T) ₂	S ₁	3.01 (412)	0.707	H-2→L+1 (37%) H-3→L (33%) H-1→L (17%)
	S ₁ '	3.03 (409)	1.118	H-2→L+1 (34%) H-2→L (16%)

				H-3→L (14%) H-1→L (10%) H-3→L+1 (9%) H→L+1 (9%) H→L (35%) H-1→L (11%) H-8→L (7%) H→L+2 (6%)
<i>r</i> -(PDI2T) ₃	S ₂	3.46 (359)	0.584	
	S ₁	3.00 (414)	0.456	H-5→L (29%) H-4→L+1 (21%) H-3→L+2 (18%) H→L (9%)
	S ₁ '	3.02 (410)	1.587	H-3→L+2 (33%) H-4→L+1 (18%) H-5→L (10%) H→L+1 (7%) H-1→L+2 (6%)
	S ₁ ''	3.03 (409)	0.793	H-3→L+2 (15%) H-5→L (13%) H-3→L (13%) H-4→L (12%) H-5→L+1 (9%)
	S ₂	3.54 (351)	0.783	H-1→L (13%) H→L (11%)
<i>i</i> -(PDI2T) ₃	S ₁	3.00 (413)	0.366	H-5→L (25%) H-4→L+1 (20%) H-3→L+2 (18%) H-1→L (11%)X
	S ₁ '	3.02 (411)	1.801	H-3→L+2 (29%) H-2→L+1 (14%) H-4→L+1 (13%) H-5→L+1 (11%) H-4→L (8%)
	S ₁ ''	3.03 (409)	0.612	H-3→L+2 (19%) H-3→L (14%) H-4→L (12%) H-1→L+2 (9%) H-5→L+1 (8%) H-2→L+1 (6%)
	S ₂	3.40 (364)	1.224	H→L (32%) H→L+3 (7%)

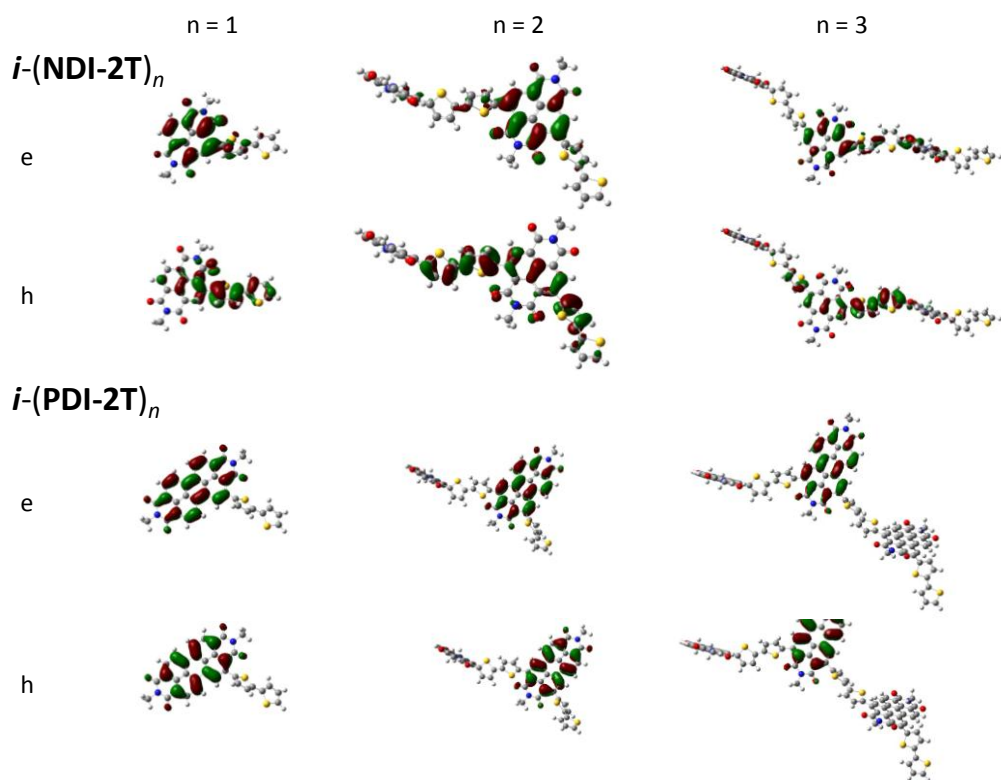


Fig. S1: Natural transition orbital (NTO) analysis for the first singlet transition ($S_0 \rightarrow S_1$) of *i*-(NDI-2T)_n and *i*-(PDI-2T)_n oligomers (e = electron, h = hole); B3LYP//B3LYP (isosurface value 0.03).

2. B3PYP results

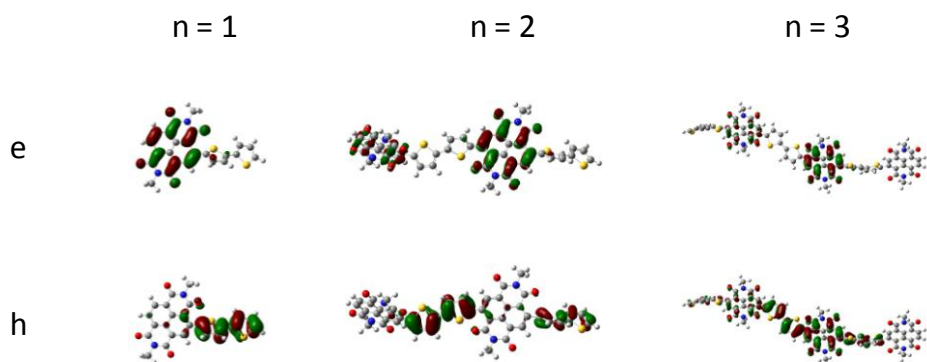


Fig. S2a: Natural transition orbital (NTO) analysis for the first singlet transition ($S_0 \rightarrow S_1$) of *r*-(NDI-2T)_n oligomers (e = electron, h = hole); B3LYP//B3LYP (isosurface value 0.03).

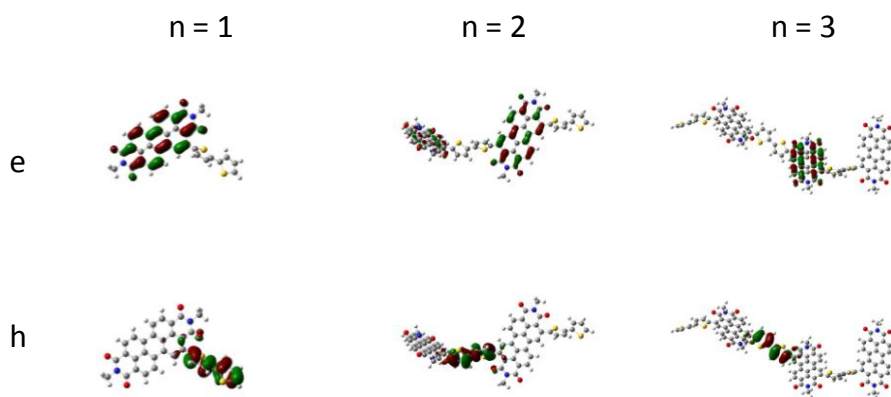


Fig. S2b: Natural transition orbital (NTO) analysis for the first singlet transition ($S_0 \rightarrow S_1$) of r -(PDI-2T) $_n$ oligomers (e = electron, h = hole); B3LYP//B3LYP (isosurface value 0.03).

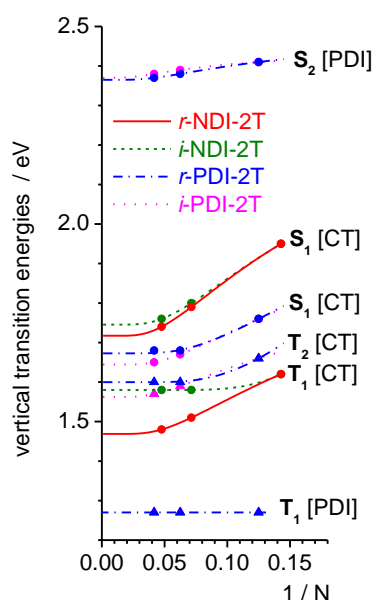


Fig. S3: Vertical transition energies of r/i -(NDI-2T) $_n$ (i.e. S_1 , T_1) and r/i -(PDI-2T) $_n$ (i.e. S_1 , S_2 , T_1 , T_2) co-oligomers, calculated at the TD-DFT (B3LYP//B3LYP) level of theory, as a function of the $1/N$. The nature of the transition is indicated in brackets (CT = charge transfer, PDI = PDI localized).

Table S2a: Vertical $S_0 \rightarrow S_1$ and $S_0 \rightarrow T_1$ electronic transition energies E with oscillator strength f , CI description (contributions $\geq 5\%$), their nature and singlet-triplet gaps of (NDI-2T) $_n$ oligomers calculated at the TD-DFT (B3LYP//B3LYP(6-311G*)) level of theory.

System	state	E / eV (λ / nm)	f	main CI configuration	nature	ΔE_{ST} / eV
(NDI2T) $_1$	T_1	1.62 (764)	—	H \rightarrow L (88%) H.2 \rightarrow L+1 (5%)	CT	0.33
	S_1	1.95 (635)	0.155	H \rightarrow L (99%)	CT	
r -(NDI2T) $_2$	T_1	1.51 (820)	—	H \rightarrow L (66%) H \rightarrow L+1 (20%)	CT	0.28
	S_1	1.79 (692)	0.585	H \rightarrow L (85%) H \rightarrow L+1 (7%) H-1 \rightarrow L (5%)	CT	
i -(NDI2T) $_2$	T_1	1.58 (783)	—	H \rightarrow L (65%) H-1 \rightarrow L (20%)	CT	0.22
	S_1	1.80 (687)	0.533	H \rightarrow L (83%) H \rightarrow L+1 (9%)	CT	

				H-1→L (5%)		
<i>r</i> -(NDI2T) ₃	T ₁	1.48 (837)	—	H→L (56%) H→L+1 (15%)	CT	0.26
	S ₁	1.74 (713)	1.054	H→L (74%) H-1→L (9%) H→L+1 (9%)	CT	
<i>i</i> -(NDI2T) ₃	T ₁	1.58 (786)	—	H→L (48%) H-1→L (25%) H-2→L+1 (8%) H-1→L+1 (6%)	CT	0.18
	S ₁	1.76 (703)	0.968	H→L (62%) H-1→L (19%) H→L+1 (5%)	CT	

Table S2b: Vertical electronic transition energies E with oscillator strengths f of **PDI-2T** oligomers calculated at the TD-DFT (B3LYP//B3LYP(6-311G*)) level of theory with CI description (contributions $\geq 5\%$): lowest singlet and triplet states with CT character, lowest PDI-localized triplet states, most intense singlet transitions ($f > 0.2 f_{\max}$); singlet-triplet gaps

System	state	E / eV (λ / nm)	f	main CI configuration	nature	ΔE_{ST} / eV
(PDI2T) ₁	T ₁	1.27 (977)	—	H-1→L (94%)	PDI	1.14
	T ₂	1.66 (745)	—	H→L (91%)	CT	0.10
	S ₁	1.76 (703)	0.052	H→L (99%)	CT	
	S ₂	2.41 (514)	0.684	H-1→L (99%)	PDI	
<i>r</i> -(PDI2T) ₂	T ₁	1.27 (978)	—	H-2→L+1 (74%) H-2→L (18%)	PDI	1.11
	T ₃	1.60 (773)	—	H→L (79%) H→L+1 (7%)	CT	0.08
	S ₁	1.68 (737)	0.136	H→L (97%)	CT	
	S ₆	2.38 (522)	0.340	H-3→L (75%) H-3→L+1 (18%)	PDI	
	S ₇	2.39 (519)	0.380	H-3→L+1 (55%) H-2→L+1 (39%)	PDI	
	S ₈	2.42 (512)	0.750	H-3→L (17%) H-3→L+1 (27%) H-2→L (10%) H-2→L+1 (46%)	PDI	
<i>i</i> -(PDI2T) ₂	T ₁	1.27 (977)	—	H-2→L (38%) H-3→L (33%) H-2→L+1 (16%) H-3→L+1 (9%)	PDI	1.12
	T ₃	1.59 (782)	—	H→L (49%) H→L+1 (42%)	CT	0.08
	S ₁	1.67 (743)	0.188	H→L (81%) H→L+1 (12%)	CT	
	S ₇	2.39 (519)	0.529	H-2→L+1 (67%) H-3→L (18%) H-3→L+1 (11%)	PDI	
<i>r</i> -(PDI2T) ₃	T ₁	1.27 (978)	—	H-3→L+1 (70%) H-3→L (11%) H-3→L+2 (10%)	PDI	1.10
	T ₄	1.60 (774)	—	H→L (62%) H-1→L (19%)	CT	0.08

	S ₁	1.68 (738)	0.1826	H→L+1 (9%) H→L (80%) H→L+1 (13%) H-1→L (5%)	CT	
	S ₁₂	2.37 (524)	0.4494	H-5→L+1 (62%) H-4→L+2 (18%) H-3→L+1 (6%) H-4→L+1 (6%)	PDI	
<i>i</i> -(PDI2T) ₃	T ₁	1.27 (978)	—	H-4→L+1 (59%) H-4→L (23%)	PDI	1.10
	T ₄	1.57 (790)	—	H→L (62%) H→L+1 (18%) H-1→L+2 (7%) H-1→L (5%)	CT	0.08
	S ₁	1.65 (751)	0.3627	H→L (70%) H→L+1 (14%) H-1→L (6%) H-1→L+2 (5%)	CT	
	S ₁₂	2.37 (524)	0.1742	H-5→L+1 (53%) H-5→L (22%) H-4→L+1 (9%)	PDI	

3. TDA-B3LYP results and comparison to TD-M06HF

Here we present TDA-B3LYP results, and a comparison with TD-M06HF for the evolution of S₁ transition energies with chain length. While B3LYP has been shown to overestimate the chain length dependence in transition energies for many oligomeric series (including oligothiophenes),^D and M06HF has been shown to provide slopes in better agreement with experiments,^D it would seem that in this particular case, the monomer-polymer shift in S₁ for *r*-(*i*-) **NDI-2T** predicted by the two functionals is quite similar; M06HF yields a shift of -0.33 (0.24) eV, and surprisingly, B3LYP yields a smaller shift of -0.27 (0.24) eV. The equivalent shift for T₁ according to TDA-B3LYP is smaller at just -0.15 (0.06) eV, consistent with the fact that triplets are normally more localized than singlets. Hence, though we expect that for many polymers (including oligothiophenes), extrapolated B3LYP S₁ energies would be more severely underestimated than T₁ energies, and hence S₁-T₁ gaps would likely be underestimated, in the specific case of the polymers studied here, this does not seem to be the case. If anything, the contrary may be true; if we trust M06HF to provide more accurate chain length dependence (in this case a stronger chain length dependence than B3LYP), this would suggest B3LYP S₁-T₁ gaps could be slightly underestimated (but by small amounts of 0.06 (0.01) eV).

Table S3: Singlet-triplet gaps as calculated at the TDA-DFT (B3LYP//B3LYP(6-311G*)) level of theory. The last two rows are extrapolated polymer values.

System	TDA-B3LYP			TD-M06HF
	S ₁ (eV)	T ₁ (eV)	ST (eV)	S ₁ (eV)
(NDI2T) ₁	2.00	1.67	0.33	3.41
<i>r</i> -(NDI2T) ₂	1.82	1.56	0.26	3.22
<i>i</i> -(NDI2T) ₂	1.83	1.62	0.2	3.29
<i>r</i> -(NDI2T) ₃	1.76	1.54	0.23	3.14
<i>i</i> -(NDI2T) ₃	1.78	1.62	0.17	3.23
<i>r</i> -P(NDI2T)	1.74	1.53	0.21	3.08
<i>i</i> -P(NDI2T)	1.77	1.61	0.15	3.17

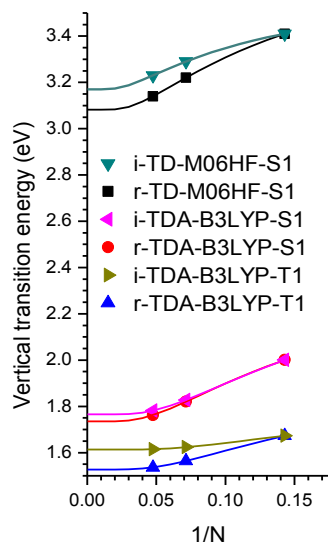


Fig. S4: Singlet and triplet vertical transition energies of *r/i*NDI-2T co-oligomers, as calculated at the TDA-DFT (B3LYP//B3LYP) and TD-DFT (M06HF//B3LYP) levels of theory, as a function of the $1/N$.

4. CAM-B3LYP results

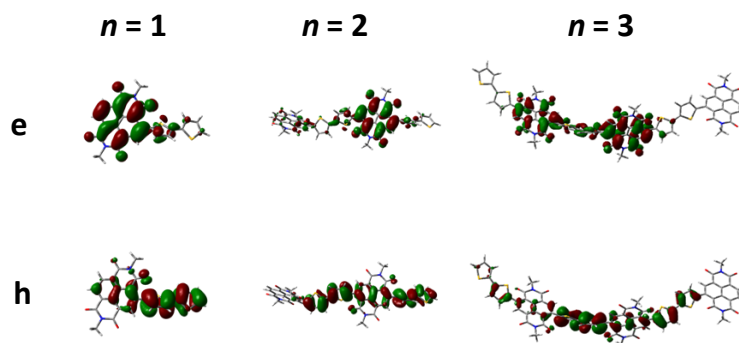


Fig. S5a: Natural transition orbital (NTO) analysis for the first singlet transition ($S_0 \rightarrow S_1$) of r -(NDI-2T) $_n$ oligomers (e = electron, h = hole); CAM-B3LYP//B3LYP (isosurface value 0.03).

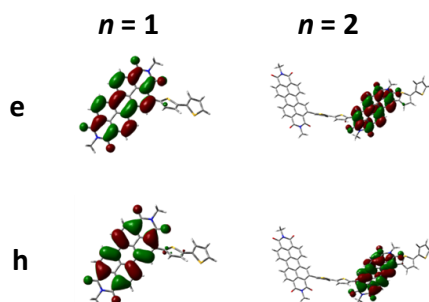


Fig. S5b: Natural transition orbital (NTO) analysis for the first singlet transition ($S_0 \rightarrow S_1$) of r -(PDI-2T) $_n$ oligomers (e = electron, h = hole); CAM-B3LYP//B3LYP (isosurface value 0.03).

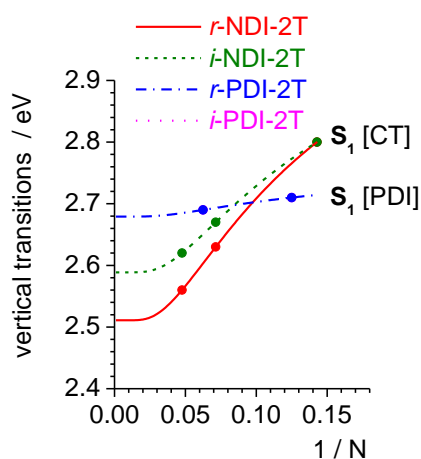


Fig. S6: Vertical $S_0 \rightarrow S_1$ transition energies s in r/i -(NDI-2T) $_n$ and (PDI-2T) $_n$ co-oligomers, calculated at the TD-DFT (CAM-B3LYP//B3LYP) level of theory, as a function of the inverse of the conjugated path length ($1/N$), where N is the conjugated path, i.e. the number of double bonds along the shortest path between the terminal C-atoms. Solid lines are exponential fits to the calculated values. The nature of the transition is indicated in brackets (CT = charge transfer, PDI = PDI localized).

Table S4a: Vertical $S_0 \rightarrow S_1$ electronic transition energies E with oscillator strength f , CI description (contributions $\geq 5\%$) of **(NDI-2T)_n** oligomers calculated at the TD-DFT (CAM-B3LYP//B3LYP(6-311G*)) level of theory.

System	state	E / eV (λ / nm)	f	main CI configuration
(NDI2T) ₁	S ₁	2.81 (442)	0.251	H→L (88%) H-4→L (5%)
<i>r</i> -(NDI2T) ₂	S ₁	2.63 (472)	0.853	H→L (77%) H-1→L+1 (5%)
<i>i</i> -(NDI2T) ₂	S ₁	2.67 (464)	0.847	H→L (76%) H-1→L+1 (7%)
<i>r</i> -(NDI2T) ₃	S ₁	2.56 (484)	1.596	H→L (60%) H-1→L+1 (13%)
<i>i</i> -(NDI2T) ₃	S ₁	2.62 (473)	1.547	H→L (60%) H-1→L+1 (15%)

Table S4b: Vertical $S_0 \rightarrow S_1$ electronic transition energies E with oscillator strength f , CI description (contributions $\geq 5\%$) of **(PDI-2T)_n** oligomers calculated at the TD-DFT (CAM-B3LYP//B3LYP(6-311G*)) level of theory.

System	state	E / eV (λ / nm)	f	main CI configuration
(PDI2T) ₁	S ₁	2.71 (458)	0.758	H-1→L (84%) H→L (14%)
<i>r</i> -(PDI2T) ₂	S ₁	2.69 (461)	0.771	H-3→L (53%) H-2→L+1 (35%) H-1→L (6%)
<i>i</i> -(PDI2T) ₂	S ₁	2.69 (461)	0.709	H-3→L (39%) H-2→L+1 (32%) H-1→L (13%)
<i>r</i> -(PDI2T) ₃	S ₁	2.68 (462)	0.510	H-5→L (44%) H-4→L+1 (28%) H-3→L+2 (18%)

5. Calculated Absorption Spectra

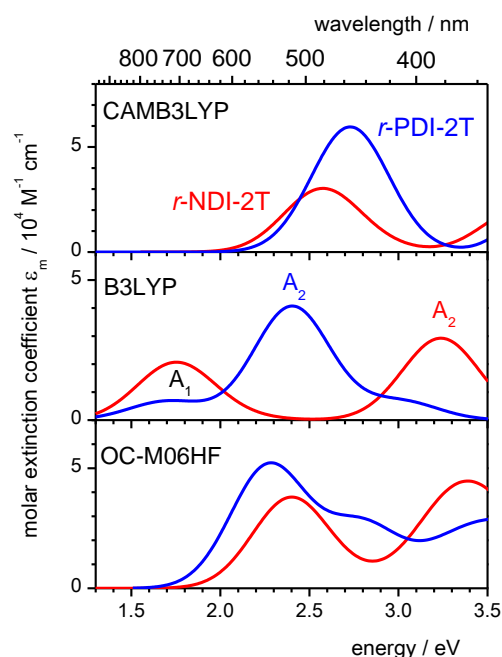


Fig. S7: TD-DFT calculated absorption spectra for $(\text{NDI-2T})_3$ and $(\text{PDI-2T})_2$, based on B3LYP optimized geometries (pure vertical transitions, broadened by Gaussians of 0.25 eV width); given in units of molar extinction coefficient per repetition units.

References

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