Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Constructing high-performance TADF polymers from non-TADF monomers: a computation investigation

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Contents

Table S4 Calculated maximum absorption/emission wavelengths, oscillator strengths, and transition characters for the investigated materials.

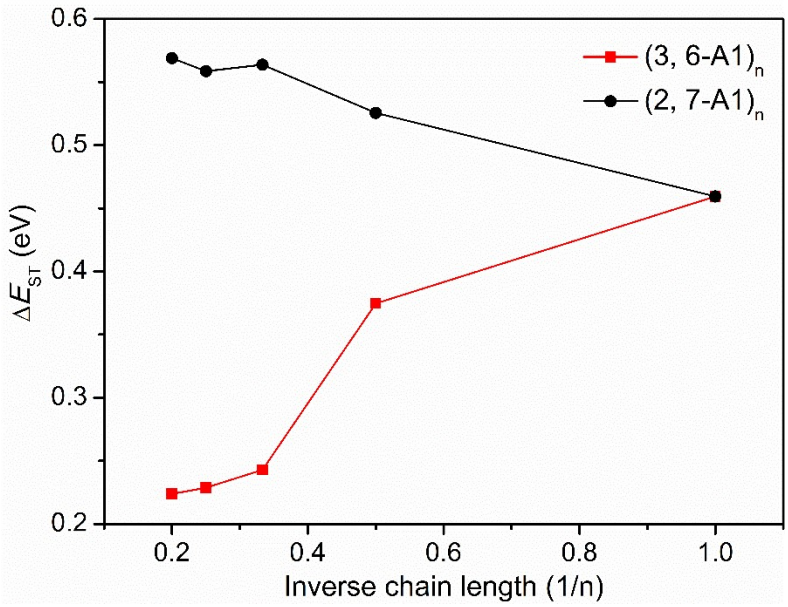
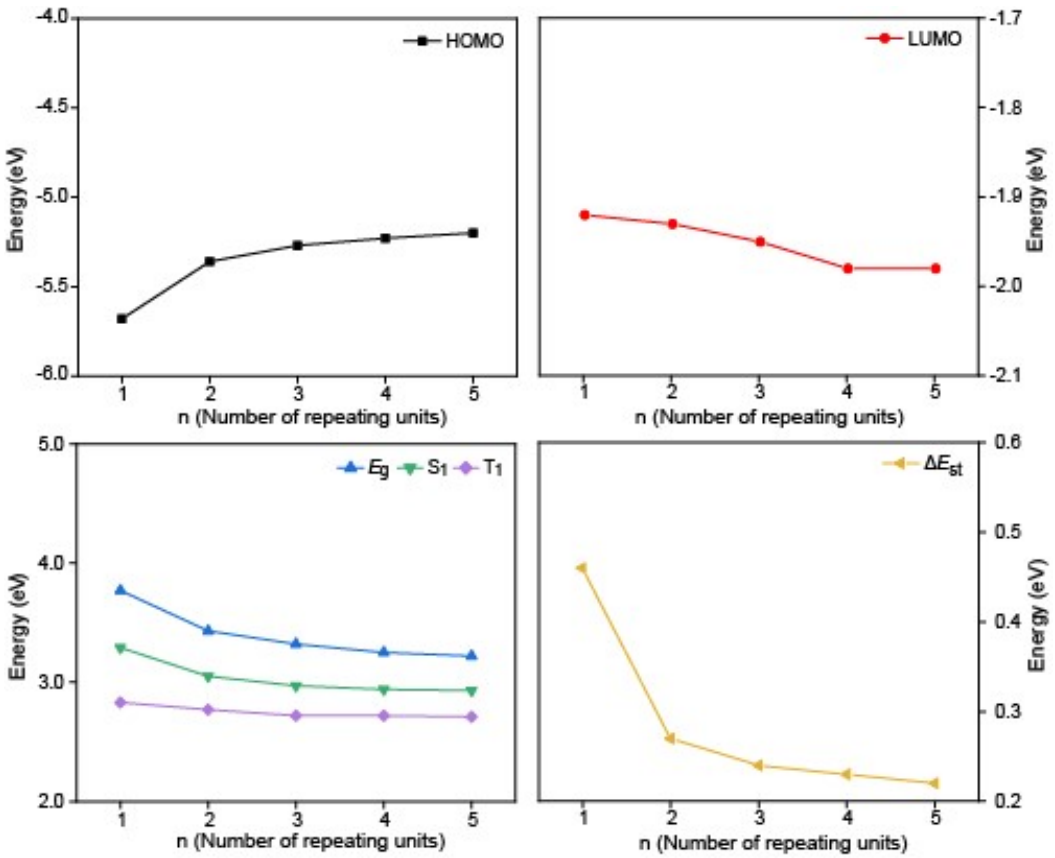


Fig. S1 Predicted ΔE_{ST} values of oligomers of A1 with different chain length polymerized at 3, 7-sties or 2, 7-sites.



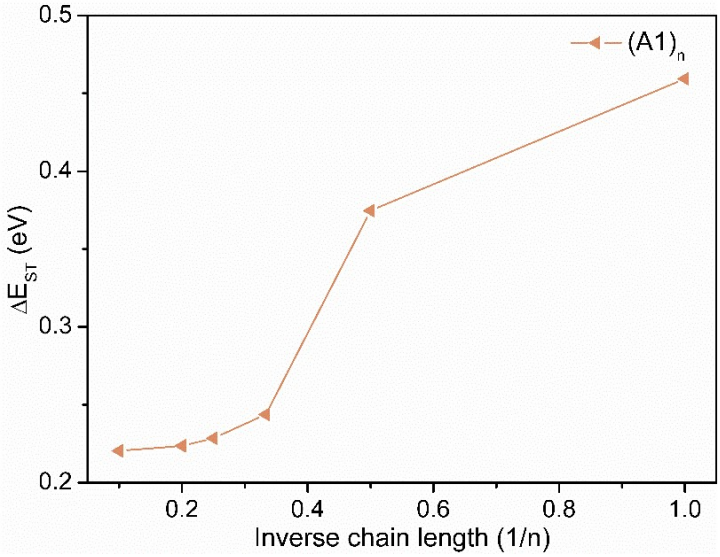
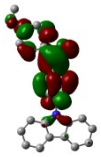
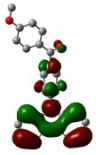
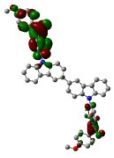
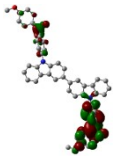
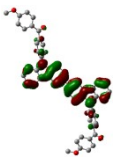
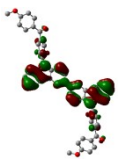


Fig. S2 Predicted HOMO/LUMO energy levels, S_1/T_1 excited energies and ΔE_{ST} values for oligomers with different numbers of repeating units (A1) at B3LYP/ def2sv levels.

n=1	 LUMO -1.92 eV				
	 HOMO -5.68 eV				
n=2	 LUMO -1.93 eV	 LUMO+1 -1.91 eV			
	 HOMO	 HOMO-1			

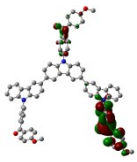
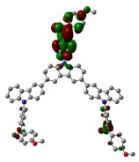
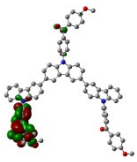
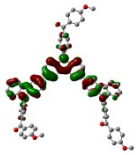
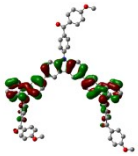
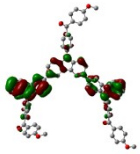
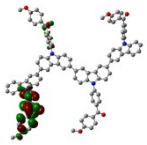
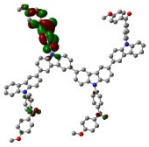
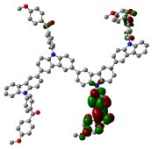
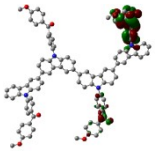
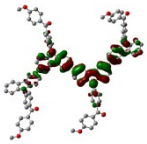
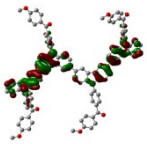
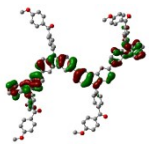
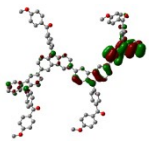
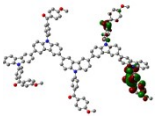
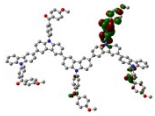
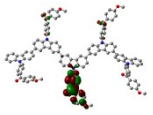
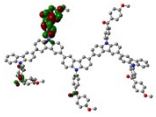
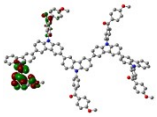
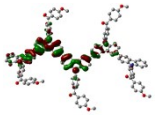
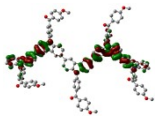
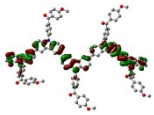
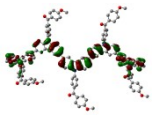
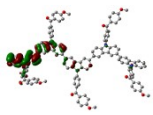
	-5.36 eV	-5.87 eV			
n=3	 LUMO -1.95 eV	 LUMO+1 -1.92 eV	 LUMO+2 -1.89 eV		
	 HOMO -5.27 eV	 HOMO-1 -5.55 eV	 HOMO-2 -5.92 eV		
n=4	 LUMO -1.98 eV	 LUMO+1 -1.94 eV	 LUMO+2 -1.90 eV	 LUMO+3 -1.87 eV	
	 HOMO -5.23 eV	 HOMO-1 -5.41 eV	 HOMO-2 -5.66 eV	 HOMO-3 -5.93 eV	
n=5	 LUMO -1.98 eV	 LUMO+1 -1.96 eV	 LUMO+2 -1.92 eV	 LUMO+3 -1.90 eV	 LUMO+4 -1.87 eV
	 HOMO -5.20 eV	 HOMO-1 -5.34 eV	 HOMO-2 -5.52 eV	 HOMO-3 -5.72 eV	 HOMO-4 -5.93 eV

Fig. S3 The electron-density distribution of oligomers with different numbers of repeating units (A1).

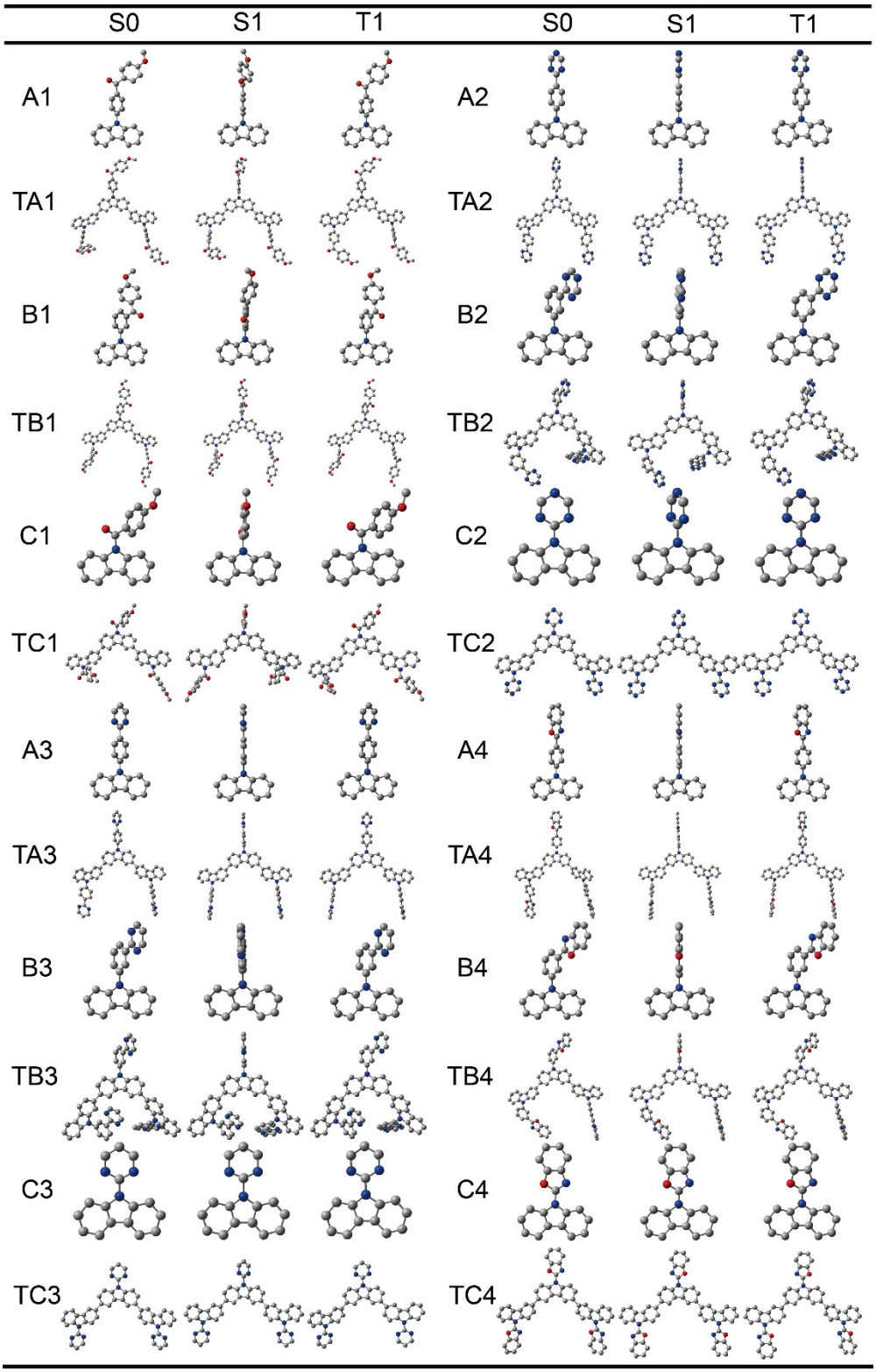


Fig. S4 Optimized ground-state and lowest-lying excited state geometry structures of the monomers and the trimers.

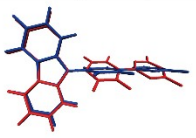
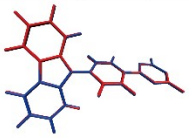
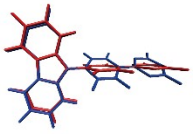
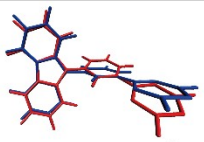
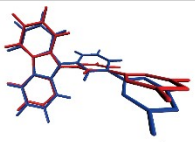
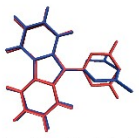
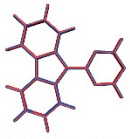
Material	S_0 *Vs* S_1	S_0 *Vs* T_1	S_1 *Vs* T_1
A2			
	RMSD=0.57 Å	RMSD=0.04 Å	RMSD=0.60 Å
TA2	RMSD=0.55 Å	RMSD=0.53 Å	RMSD=0.02 Å
B2			
	RMSD=0.66 Å	RMSD=0.17 Å	RMSD=0.82 Å
TB2	RMSD=0.93 Å	RMSD=0.63 Å	RMSD=0.59 Å
C2			
	RMSD=0.61 Å	RMSD=0.03 Å	RMSD=0.61 Å
TC2	RMSD=0.48 Å	RMSD=0.89 Å	RMSD=0.82 Å

Fig. S5 Geometry variations between S_0, S_1 and T_1 states of A2, B2 and C2 as well as the trimers of TA2, TB2 and TC2.

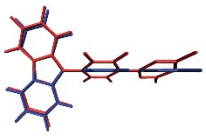
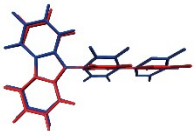
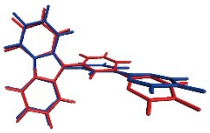
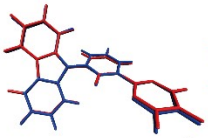
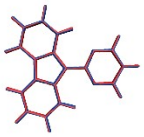
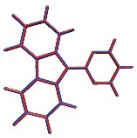
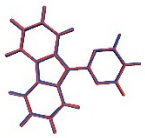
Material	S_0 *Vs* S_1	S_0 *Vs* T_1	S_1 *Vs* T_1
A3			
	RMSD=0.55 Å	RMSD=0.07 Å	RMSD=0.62 Å
TA3	RMSD=0.57 Å	RMSD=0.14 Å	RMSD=0.51 Å
B3			
	RMSD=0.61 Å	RMSD=0.23 Å	RMSD=0.82 Å
TB3	RMSD=0.68 Å	RMSD=0.12 Å	RMSD=0.77 Å
C3			
	RMSD=0.05 Å	RMSD=0.03 Å	RMSD=0.05 Å
TC3	RMSD=0.49 Å	RMSD=0.95 Å	RMSD=0.80 Å

Fig. S6 Geometry variations between S_0, S_1 and T_1 states of A3, B3 and C3 as well as the trimers of TA3, TB3 and TC3.

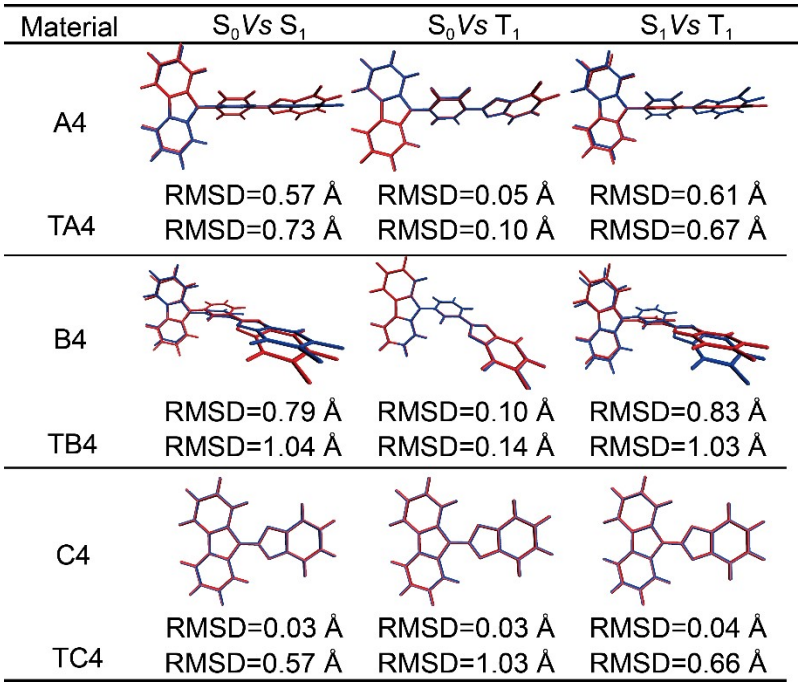


Fig. S7 Geometry variations between S_0, S_1 and T_1 states of A4, B4 and C4 as well as the trimers of TA4, TB4 and TC4.

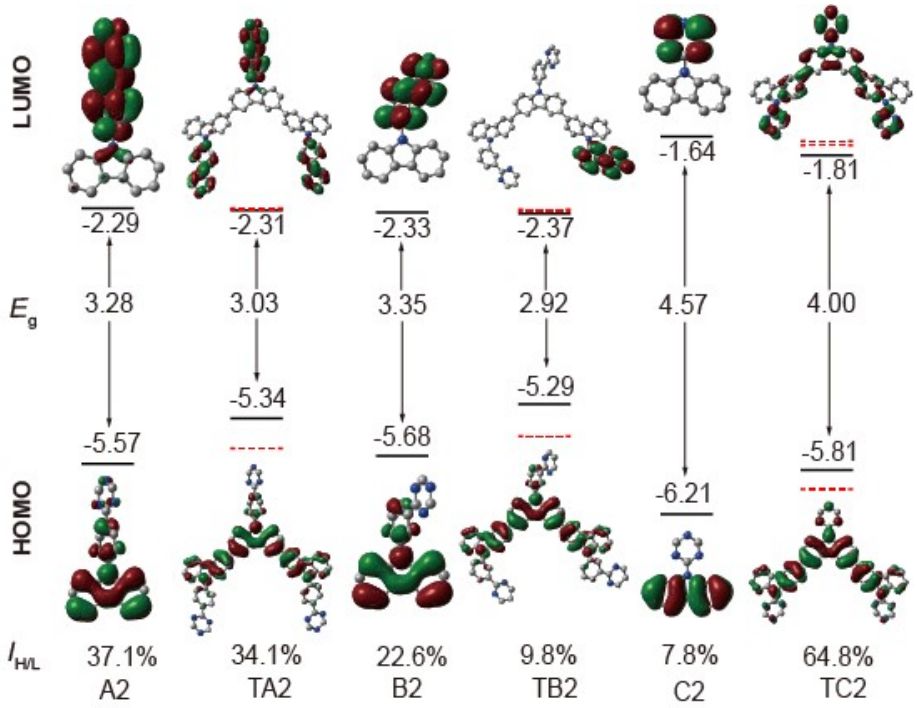


Fig. S8 Calculated frontier orbital energy levels, frontier orbitals distribution and HOMO-LUMO overlap extent ($I_{H/L}$) for A2, B2, C2 and the trimers of TA2, TB2 and TC2.

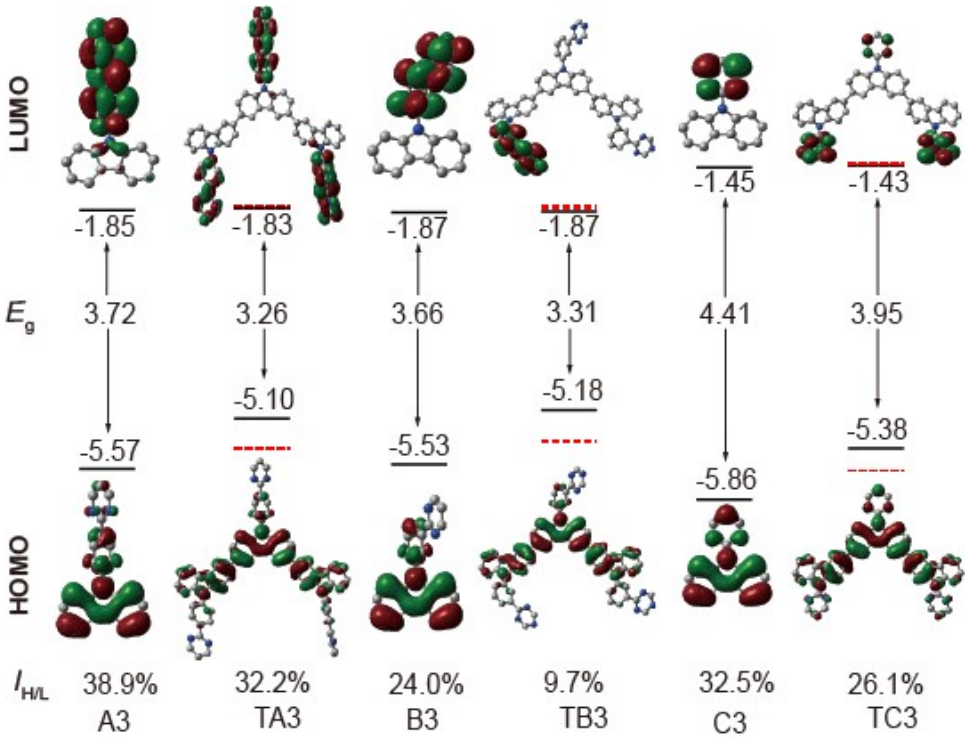


Fig. S9 Calculated frontier orbital energy levels levels, frontier orbitals distribution and HOMO-LUMO overlap extent ($I_{H/L}$) for A3, B3, C3 and the trimers of TA3, TB3 and TC3.

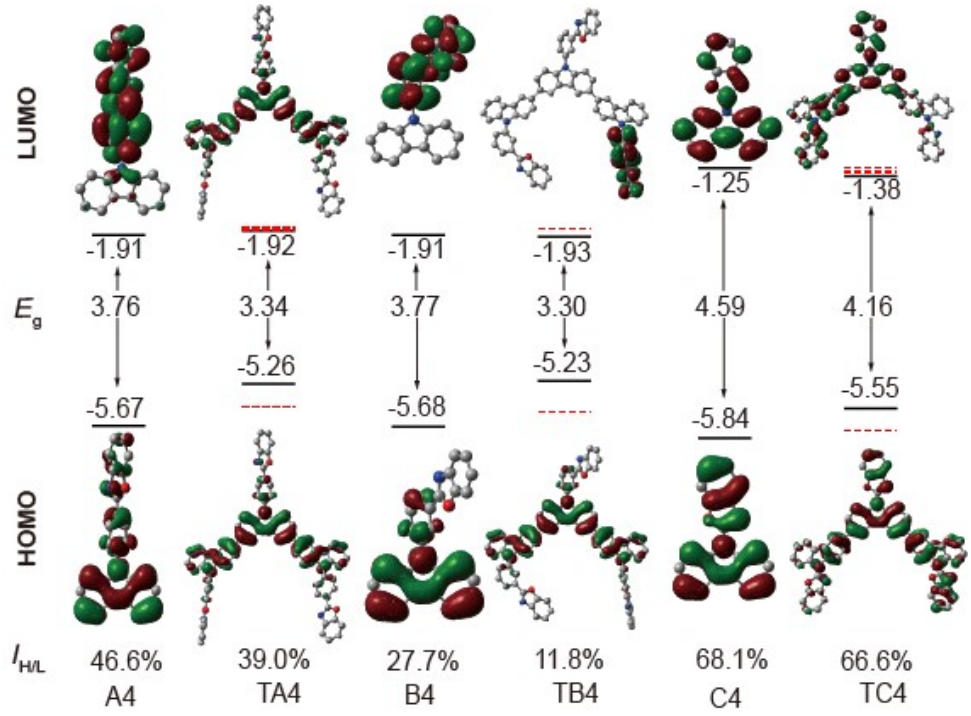


Fig. S10 Calculated frontier orbital energy levels levels, frontier orbitals distribution and HOMO-LUMO overlap extent ($I_{H/L}$) for A4, B4, C4 and the trimers of TA4, TB4 and TC4.

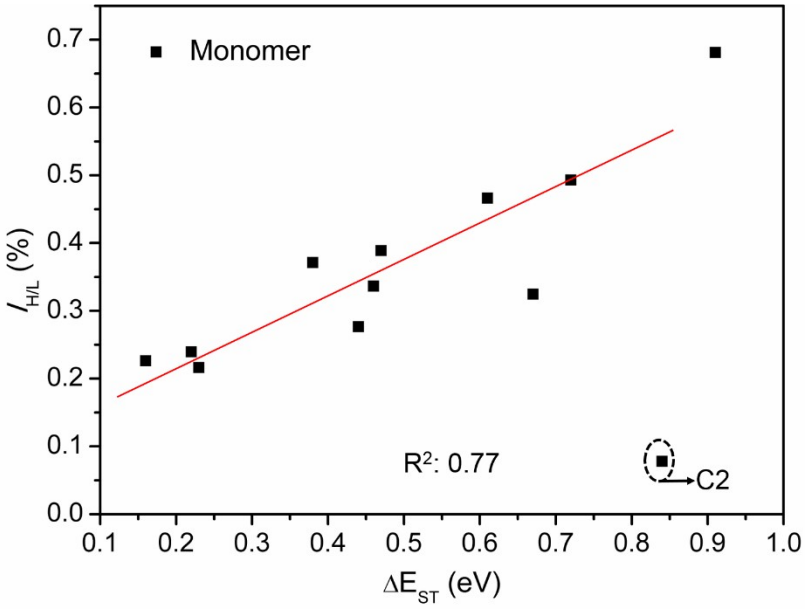


Fig. S11 Correlation between singlet-triplet energy splitting (ΔE_{ST}) and HOMO-LUMO overlap extent ($I_{H/L}$) for the investigated monomers except for C2.

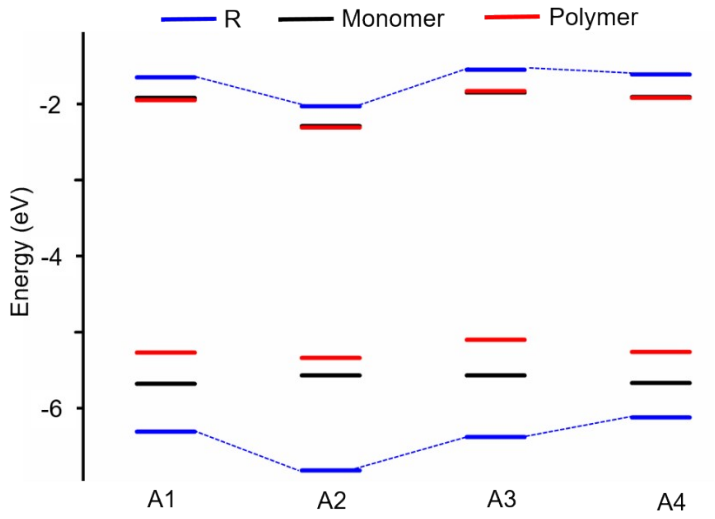


Fig. S12 Calculated HOMO energy levels for the investigated monomers, polymers and their corresponding R units of series A.

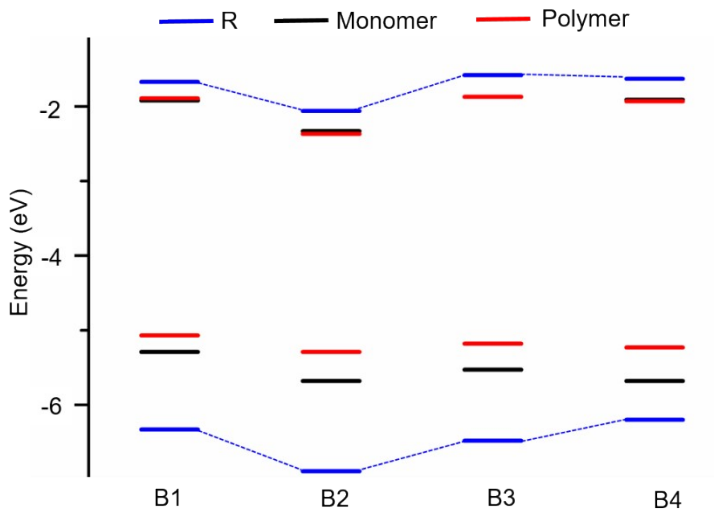


Fig. S13 Calculated HOMO energy levels for the investigated monomers, polymers and their corresponding R units of series B.

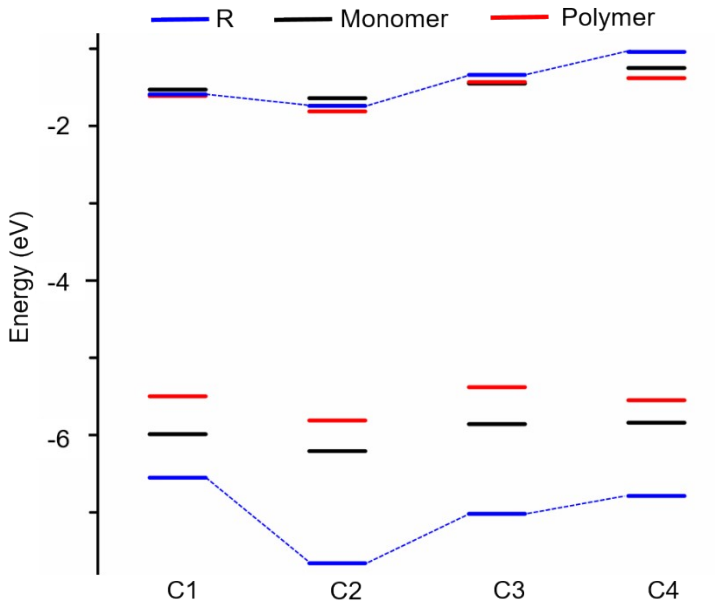


Fig. S14 Calculated HOMO energy levels for the investigated monomers, polymers and their corresponding R units of series C.

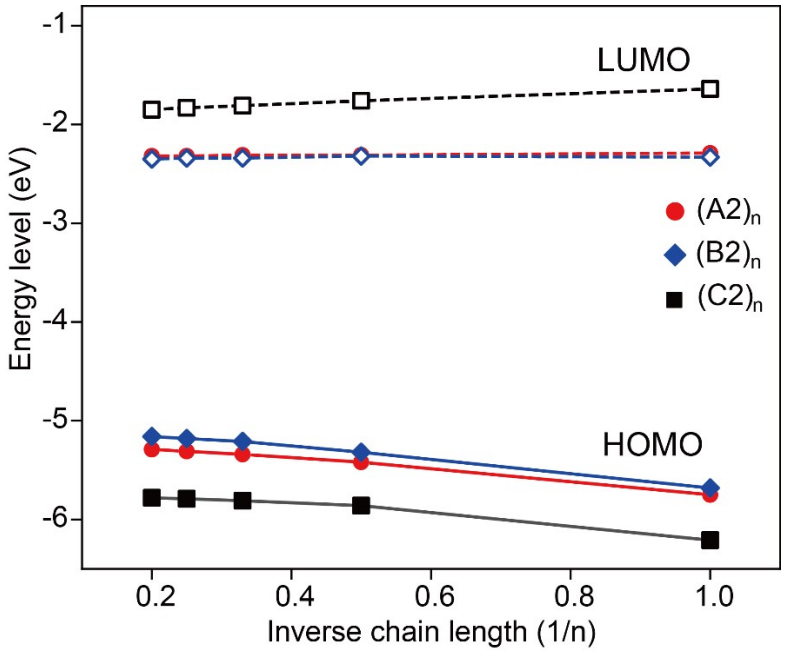


Fig. S15 Linear relation between the HOMO and LUMO energy levels and reciprocal chain length of oligomers.

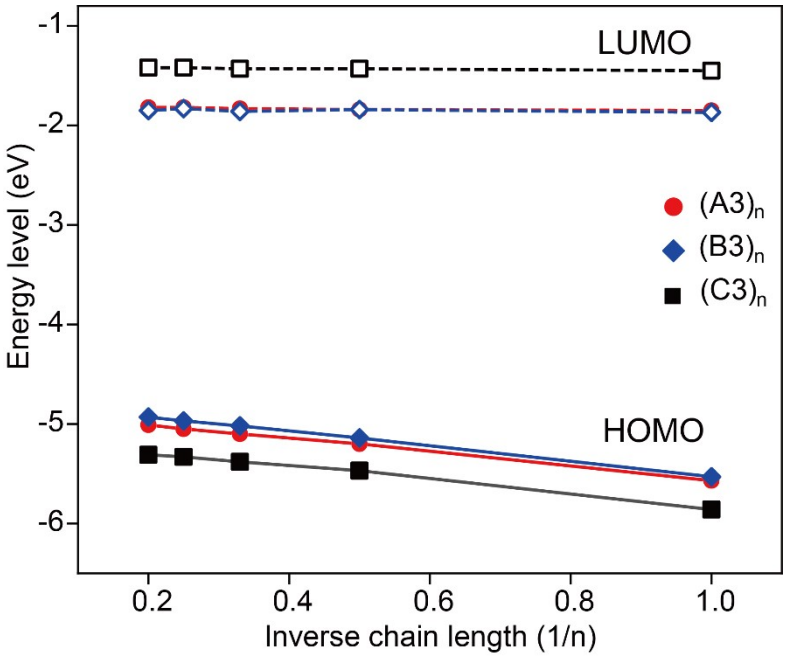


Fig. S16 Linear relation between the HOMO and LUMO energy levels and reciprocal chain length of oligomers.

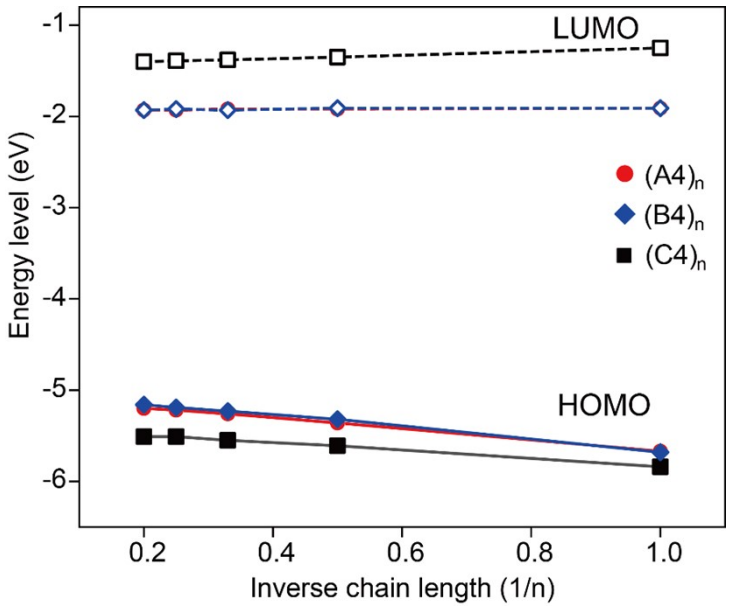


Fig. S17 Linear relation between the HOMO and LUMO energy levels and reciprocal chain length of oligomers.

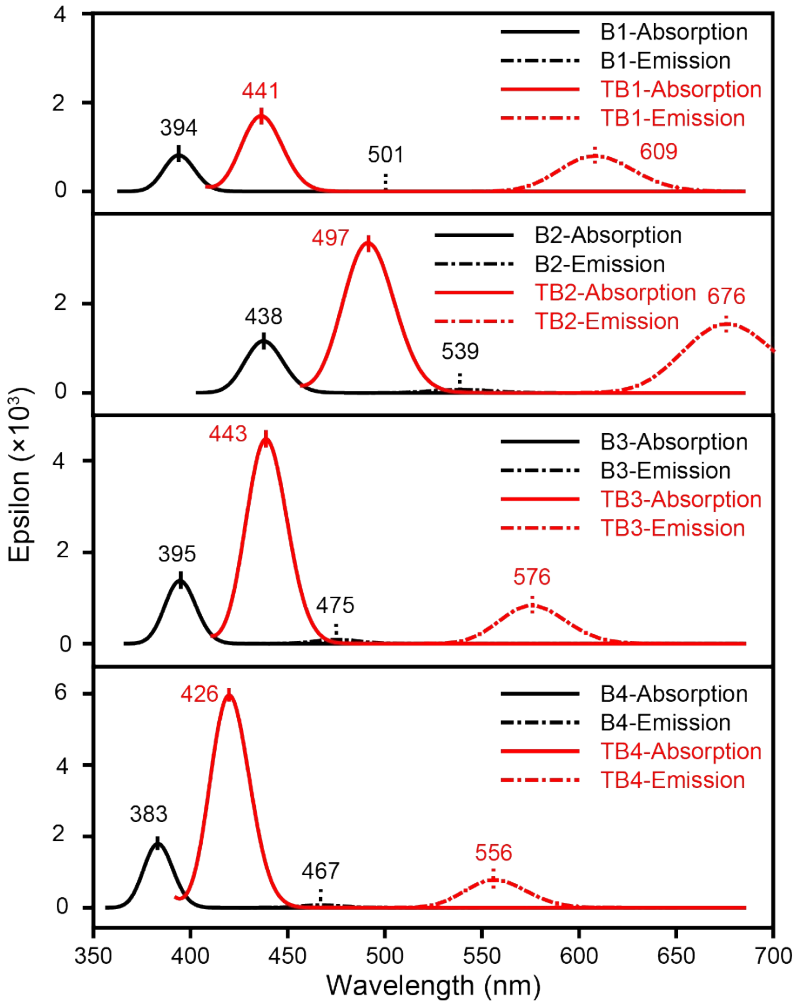


Fig. S18 Simulated absorption and emission spectra of B1-B4 and their trimers of TB1-TB4.

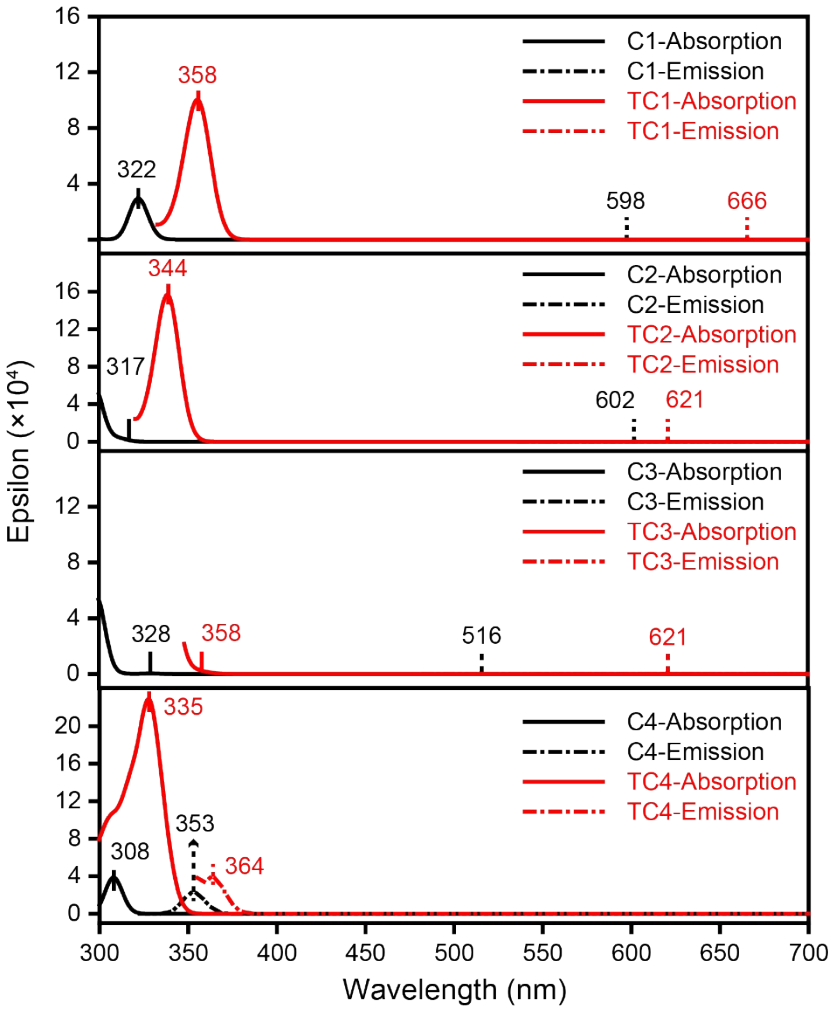


Fig. S19 Simulated absorption and emission spectra of C1-C4 and their trimers of TC1-TC4.

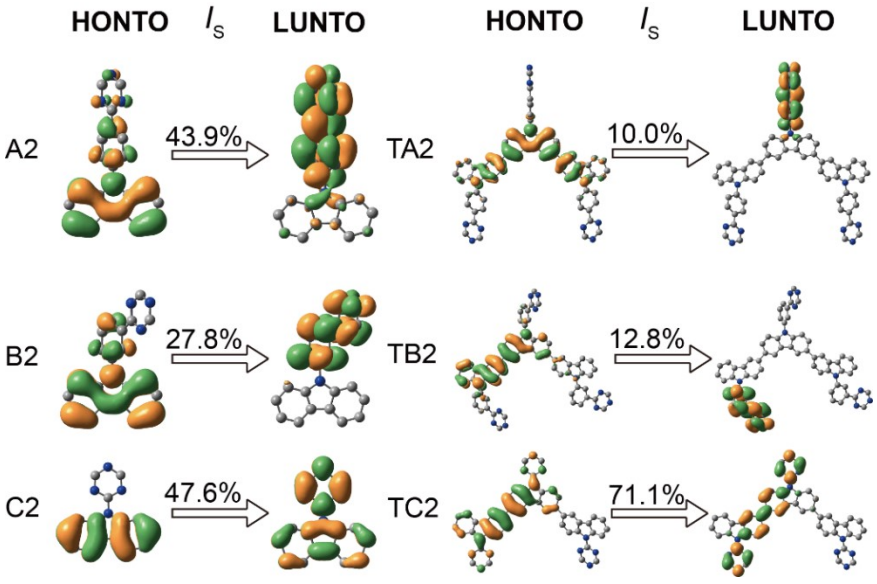


Fig. S20 NTO distributions and overlap extents (I_s) at S_1 states for the A2, B2, C2 and the trimers of TA2, TB2 and TC2.

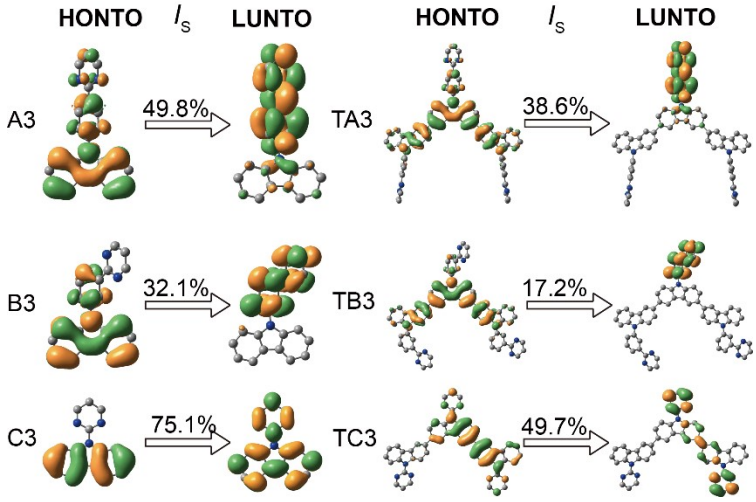


Fig. S21 NTO distributions and overlap extents (I_s) at S_1 states for the A3, B3, C3 and the trimers TA3, TB3 and TC3.

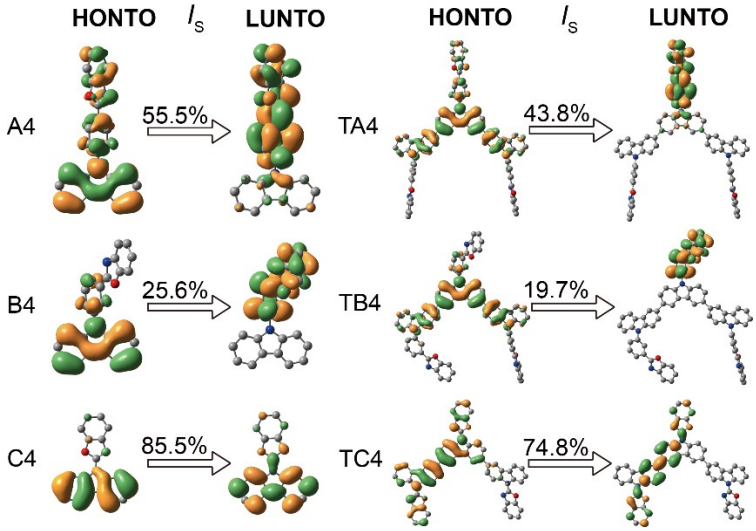


Fig. S22 NTO distributions and overlap extents (I_s) at S_1 states for the A4, B4, C4 and the trimers of TA4, TB4 and TC4.

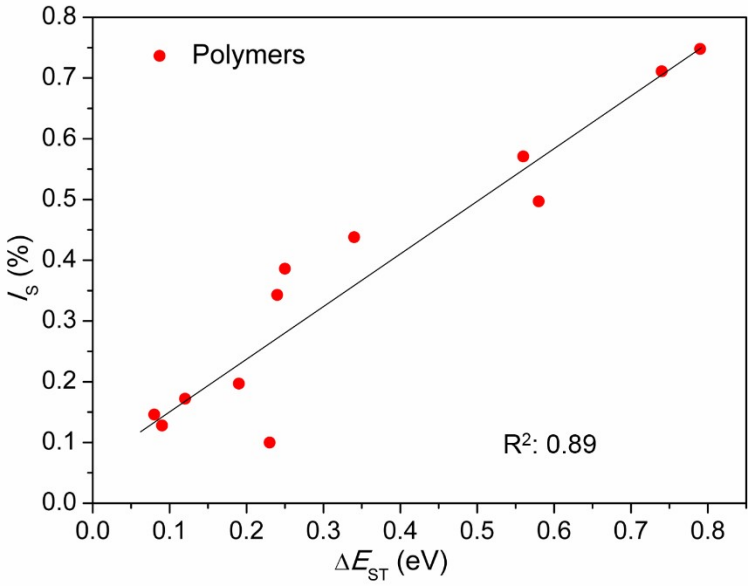


Fig. S23 Correlation between singlet-triplet energy splitting (ΔE_{ST}) and HONTO-LUNTO overlap extent (I_s) for the investigated polymers.

Table S1 Calculated frontier orbital energy levels, band gaps, excited-state energies and ΔE_{ST} values with different DFT functionals for A1 and its oligomers (Unit: eV).

Functional	Number of repeating units	HOMO	LUMO	E_g	S_1	T_1	ΔE_{ST}
B3LYP	n=1	-5.68	-1.92	3.77	3.29	2.83	0.46
	n=2	-5.36	-1.93	3.43	3.05	2.77	0.27
	n=3	-5.27	-1.95	3.32	2.97	2.72	0.24
	n=4	-5.23	-1.98	3.25	2.94	2.72	0.23
	n=5	-5.20	-1.98	3.22	2.93	2.71	0.22
B3LYP+D3	n=1	-5.68	-1.90	3.79	3.31	2.83	0.48
	n=2	-5.36	-1.92	3.45	3.06	2.77	0.29
	n=3	-5.27	-1.94	3.33	3.04	2.72	0.32
	n=4	-5.23	-1.96	3.27	2.96	2.72	0.24
	n=5	-5.21	-1.97	3.24	2.96	2.71	0.24
BMK	n=1	-6.41	-1.23	5.18	3.72	3.06	0.66
	n=2	-6.06	-1.25	4.81	3.70	3.06	0.64
	n=3	-5.96	-1.27	4.69	3.67	3.05	0.62
	n=4	-5.91	-1.30	4.61	3.66	3.05	0.61
	n=5	-5.89	-1.30	4.58	3.66	3.05	0.61
CAMB3LYP	n=1	-6.97	-0.71	6.26	3.86	2.93	0.93
	n=2	-6.59	-0.72	5.86	3.86	2.82	1.04
	n=3	-6.49	-0.74	5.74	3.86	2.78	1.08
	n=4	-6.43	-0.77	5.66	3.85	2.75	1.10

	n=5	-6.41	-0.77	5.63	3.85	2.74	1.12
M062X	n=1	-6.92	-1.05	5.87	3.65	3.12	0.53
	n=2	-6.56	-1.07	5.48	3.65	3.13	0.52
	n=3	-6.46	-1.09	5.37	3.65	3.12	0.52
	n=4	-6.41	-1.12	5.29	3.65	3.12	0.52
	n=5	-6.38	-1.12	5.26	3.65	3.12	0.52
PBE1PBE	n=1	-5.95	-1.83	4.12	3.47	2.82	0.65
	n=2	-5.62	-1.85	3.77	3.26	2.79	0.47
	n=3	-5.54	-1.87	3.67	3.18	2.77	0.41
	n=4	-5.49	-1.90	3.59	3.16	2.76	0.40
	n=5	-5.47	-1.90	3.56	3.15	2.76	0.39
wB97XD	n=1	-7.56	-0.17	7.40	3.85	3.05	0.81
	n=2	-7.18	-0.19	6.99	3.86	2.98	0.88
	n=3	-7.08	-0.21	6.87	3.86	2.94	0.92
	n=4	-7.03	-0.23	6.79	3.86	2.92	0.94
	n=5	-7.00	-0.24	6.76	3.86	2.90	0.95
Exp.	A1	-5.96	-3.03	2.93	3.035	--	0.442
	P1	-5.66	-3.10	2.56	2.689	--	0.233

Table S2 Calculated frontier orbital energy levels, band gaps, excited-state energies and ΔE_{ST} values with different basis sets for A1 and its trimers (Unit: eV).

Material	Method	HOMO	LUMO	E_g	S_1	T_1	ΔE_{ST}
A1	B3LYP/def2sv	-5.68	-1.92	3.77	3.29	2.83	0.46
	B3LYP/def2sv+D3	-5.68	-1.90	3.79	3.31	2.83	0.48
	B3LYP/6-31+g*	-5.73	-2.06	3.66	3.19	2.81	0.38
	B3LYP/6-311g*	-5.67	-1.93	3.74	3.27	2.85	0.42
	Exp.	-5.96	-3.03	2.93	3.035	--	0.442
TA1	B3LYP/def2sv	-5.27	-1.95	3.32	2.97	2.74	0.24
	B3LYP/def2sv+D3	-5.27	-1.94	3.34	2.98	2.72	0.26
	B3LYP/6-31+g*	-5.32	-2.10	3.22	2.87	2.67	0.20
	B3LYP/6-311g*	-5.29	-1.96	3.32	2.96	2.74	0.22
	Exp.	-5.66	-3.10	2.56	2.689	--	0.233

Table S3 Selected geometrical parameters of the investigated molecules in the ground state (S_0) and the lowest singlet/triplet excited state (S_1/T_1).

Material	S_0		S_1		T_1	
	$l_{N\text{-}R}$ (Å)	φ (º)	$l_{N\text{-}R}$ (Å)	φ (º)	$l_{N\text{-}R}$ (Å)	φ (º)
A1	1.42	53.7	1.45	91.7	1.41	53.5
TA1	1.42	53.0	1.45	90.9	1.42	53.6
A2	1.41	52.2	1.45	90.0	1.41	49.2
TA2	1.41	51.7	1.45	90.4	1.45	88.7
A3	1.42	53.8	1.45	90.0	1.40	47.9
TA3	1.42	52.6	1.45	90.3	1.41	48.9
A4	1.42	53.8	1.45	90.1	1.41	50.5
TA4	1.42	52.8	1.45	90.5	1.41	49.6
B1	1.42	54.4	1.46	81.8	1.42	57.2
TB1	1.42	52.9	1.46	75.5	1.45	60.6
B2	1.42	57.0	1.46	87.8	1.42	46.8
TB2	1.42	56.1	1.46	84.3	1.45	59.4
B3	1.42	58.0	1.46	85.5	1.41	45.3
TB3	1.42	56.2	1.46	84.2	1.43	50.2
B4	1.42	57.1	1.46	90.5	1.42	55.5
TB4	1.42	55.3	1.46	89.0	1.42	52.9
C1	1.41	37.2	1.55	82.7	1.41	32.0
TC1	1.41	36.5	1.54	83.3	1.42	35.5
C2	1.38	0.0	1.51	53.1	1.38	0.0
TC2	1.38	0.2	1.50	47.1	1.39	0.2
C3	1.39	0.0	1.53	0.12	1.39	0.0
TC3	1.36	0.0	1.50	0.38	1.39	0.2
C4	1.37	0.0	1.32	0.0	1.37	0.0
TC4	1.37	0.2	1.36	0.4	1.37	0.2

Table S4 Calculated maximum absorption/emission wavelengths ($\lambda_{abs}/\lambda_{em}$, nm), oscillator strengths (*f*), and transition characters for the investigated materials.

Material	λ_{abs}	f	Main configuratons[a]	λ_{em}	*f*	Main configurations[a]
A1	377	0.2113	H→L (0.97)	476	0.0002	H→L (0.99)
TA1	418	0.3540	H→L (0.23); H→L+1 (0.72)	575	0	H→L (0.98)
A2	410	0.2535	H→L (0.99)	524	0	H→L (0.99)
TA2	463	0.4333	H→L (0.81); H→L+2 (0.16)	634	0.0001	H→L (0.98)
A3	381	0.2628	H→L (0.99)	465	0	H→L (0.99)
TA3	428	0.4553	H→L (0.56); H→L+2 (0.36)	556	0.0001	H→L (0.98)
A4	378	0.4020	H→L (0.98)	464	0	H→L (0.99)
TA4	418	0.7293	H→L (0.85)	550	0.0002	H→L (0.98)
B1	394	0.0045	H→L (0.99)	501	0.0005	H→L (0.99)
TB1	441	0.0046	H→L+2 (0.92)	609	0.0044	H→L (0.98)
B2	438	0.0064	H→L (0.99)	539	0.0004	H→L (0.99)
TB2	497	0.0083	H→L+1 (0.59); H→L+2 (0.38)	676	0.0085	H→L (0.97)
B3	395	0.0076	H→L (0.99)	475	0.0005	H→L (0.99)
TB3	443	0.0110	H→L+2 (0.97)	576	0.0046	H→L (0.98)
B4	383	0.0099	H→L (0.99)	467	0.0004	H→L (0.99)
TB4	426	0.0132	H→L+1 (0.91)	556	0.0048	H→L (0.98)
C1	322	0.1620	H→L (0.98)	598	0	H→L (0.99)
TC1	358	0.4200	H→L (0.67); H→L+1 (0.24)	666	0	H→L (0.97)
C2	317	0.0007	H-1→L (0.99)	602	0.0002	H→L (1.00)
TC2	344	0.0195	H→L+1 (0.61); H→L+2 (0.24)	655	0.0003	H→L (0.98)
C3	329	0.0023	H→L (0.99)	516	0	H→L (1.00)
TC3	358	0.0049	H→L (0.11); H→L+2 (0.84)	621	0.0003	H→L (0.98)
C4	308	0.2133	H→L (0.90)	353	0.1240	H→L (0.97)

TC4	335	0.3914	H→L (0.58); H→L+1 (0.23)	364	0.2099	H→L (0.58)

[a] H denotes the HOMO, and L is the LUMO