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

Modeling of Photoactive Conjugated Donor–Acceptor Copolymers: The Effect of the Exact HF Exchange in DFT Functionals on Geometries and Gap Energies of Oligomer and Periodic Models

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ELECTRONIC SUPPLEMENTARY INFORMATION

Amount of the exact HF exchange in the density functionals

The PBE, M06L, B3LYP, PBE0, M06, M062X and M06HF functionals have been used to assess the amount of the effective HF exchange in the HSE06, OT-ωB97X, ωB97XD, and LC-ωPBE functionals. The effective HF exchange depends on the system so the HOCO–LUCO gaps of the P1–P3 models have been used in the assessment. The HOCO–LUCO gaps of the polymers are presented as a function of the HF exchange and a simple linear regression can be used to estimate the effective HF exchange. The plots are presented in Figures S1–S3 and Table S1 contains the amount of effective HF exchange in the HSE06, OT-ωB97X, ωB97XD, and LC-ωPBE functionals.

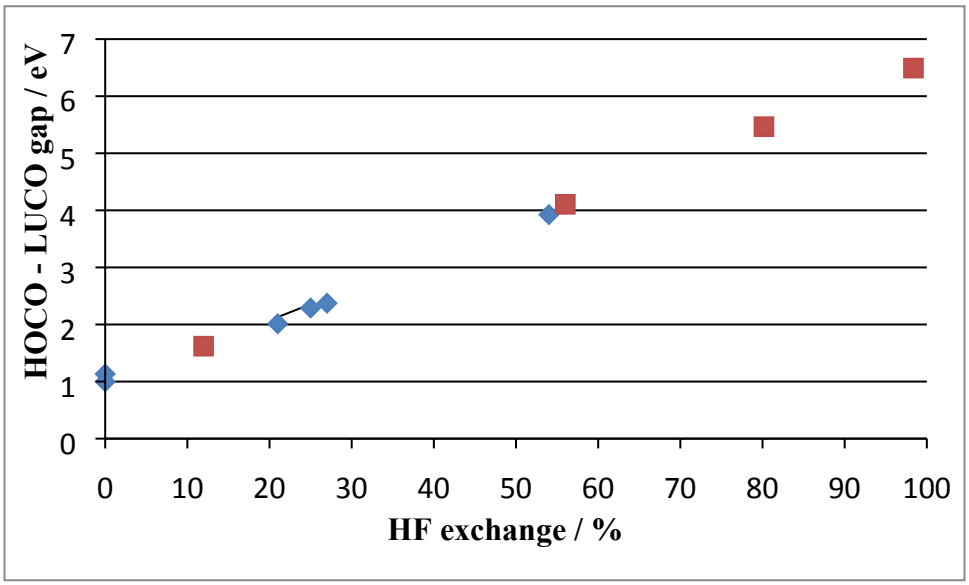

Figure S1. Assessment of the effective HF exchange in the case of polymer P1.

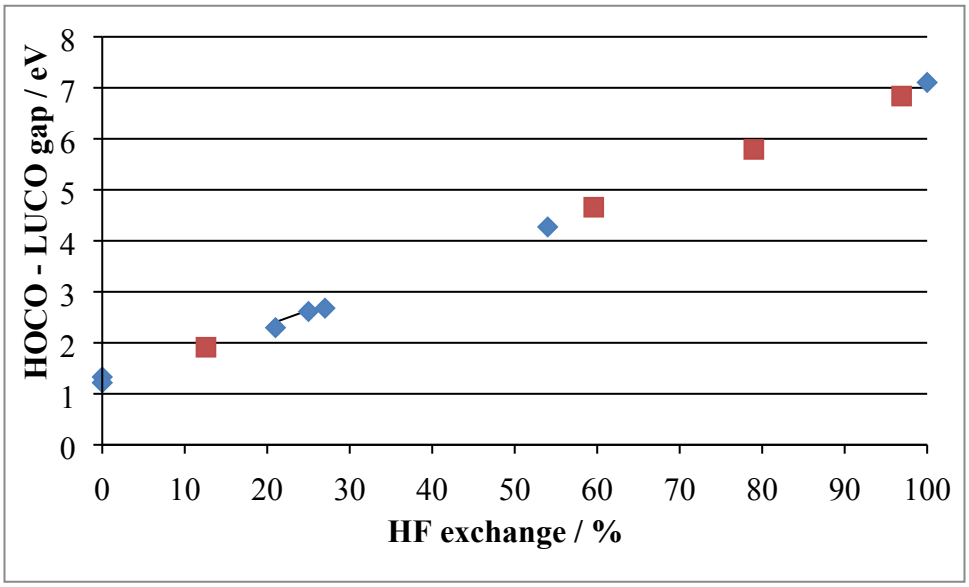

Figure S2. Assessment of the effective HF exchange in the case of polymer P2.

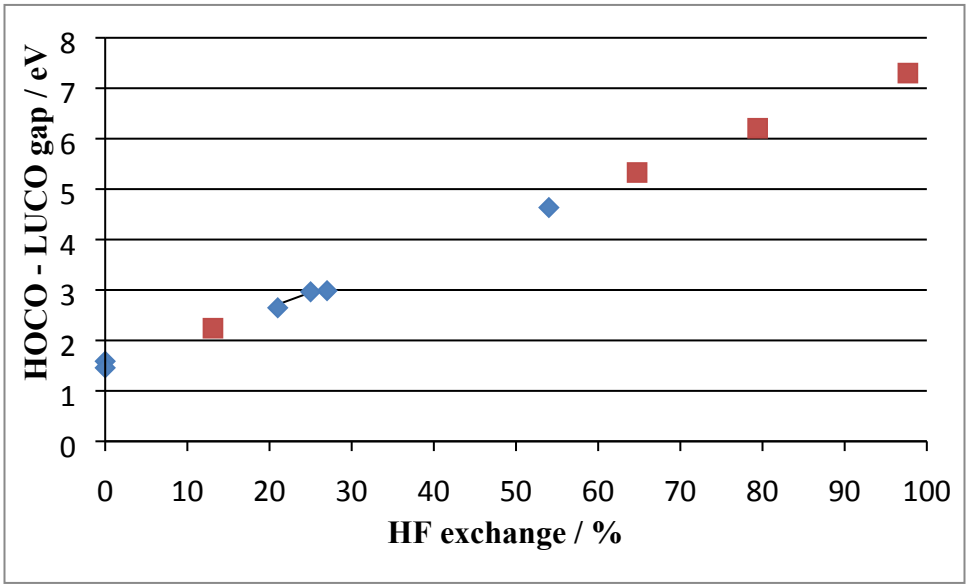

Figure S3. Assessment of the effective HF exchange in the case of polymer P3.

Table S1. Amount of the effective HF exchange in the HSE06, ωB97XD, and LC-ωPBE functionals.

	P1		P2		P3	
	H–L gap / eV	HF_{eff} / %	H–L gap / eV	HF_{eff} / %	H–L gap / eV	HF_{eff} / %
HSE06	1.620	12.0	1.913	12.6	2.242	13.1
OT-ωB97X	4.105	56.0	4.658	59.6	5.329	64.7
ωB97XD	5.466	80.2	5.792	79.0	6.207	79.4
LC-ωPBE	6.492	98.4	6.838	96.9	7.300	97.7

The amount of the effective HF exchange in the HSE06, OT-ωB97X , ωB97XD, and LC-ωPBE functionals is (12–13) %, (56–65) %, (79–80) %, and (97–98) %, respectively, in the studied systems.

Effect of the method on the bond length alternation

The path used for the bond length alternation (BLA) analysis is given in Figures S4 and S5. The bond lengths are presented visually in Figures S6–S8 and are given in Tables S2–S4. The BLA can be calculated as follows

$$BLA = \frac{\sum double\ bond\ lengths}{N_{double\ bonds}} - \frac{\sum single\ bond\ lengths}{N_{single\ bonds}},$$

where N is the number of the respective bonds. The BLA of the excited state was not analyzed because periodic models were used (and thus the TD formalism was not available).

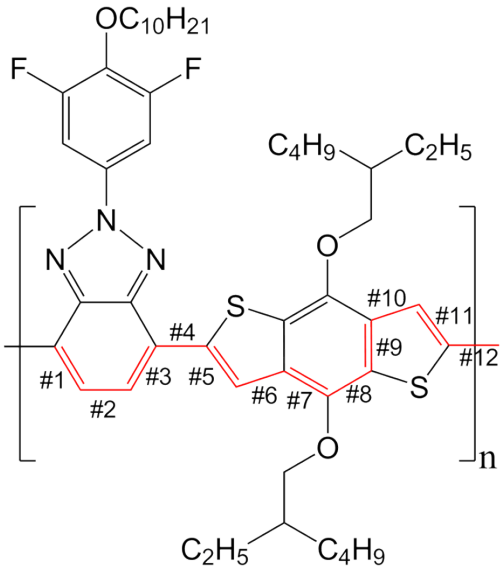

Figure S4. Bond path in P1.

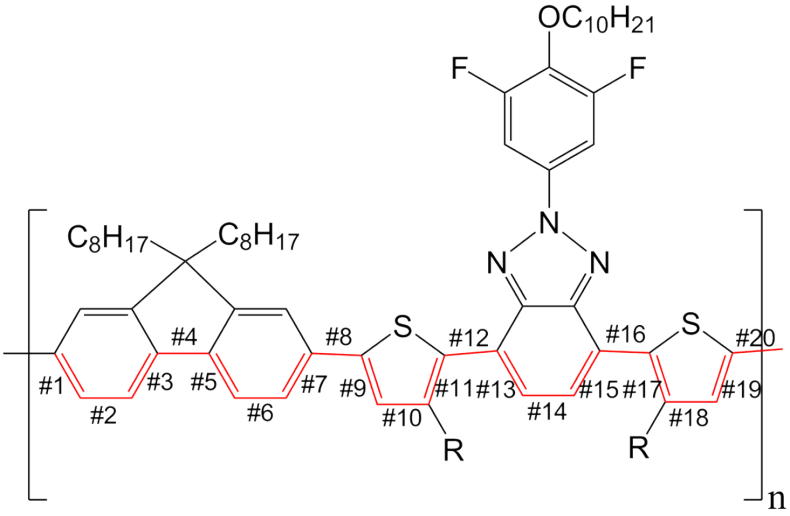

Figure S5. Bond path in P2 and P3.

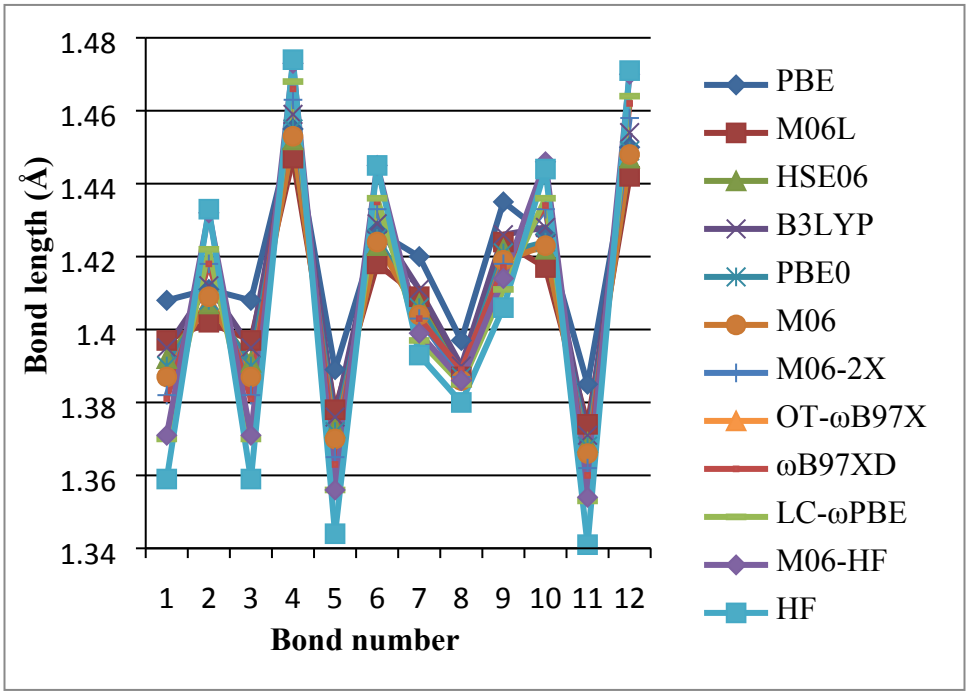

Figure S6. Bond lengths (Å) on the bond path in P1.

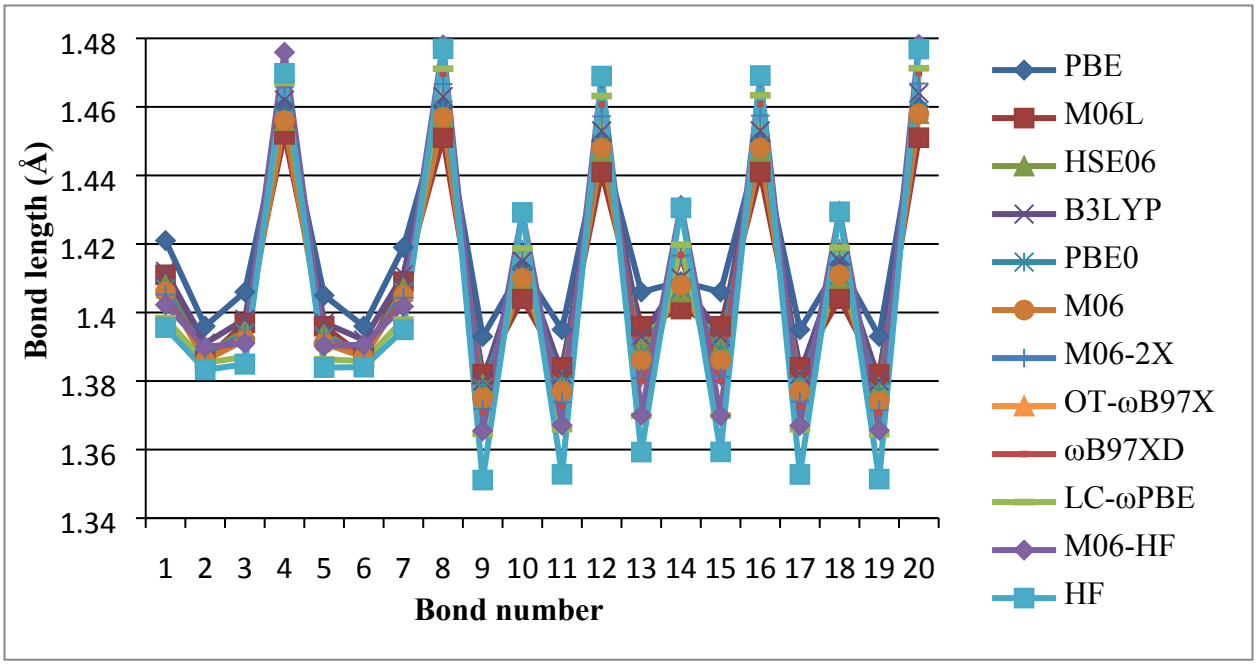

Figure S7. Bond lengths (Å) on the bond path in P2.

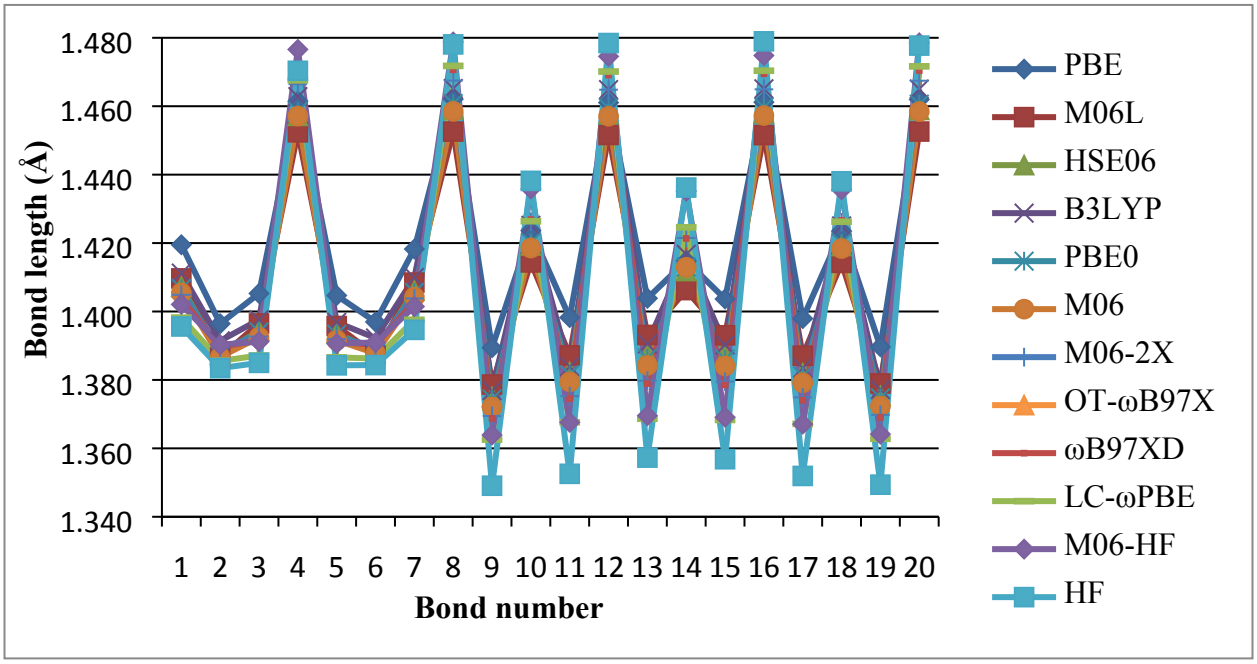

Figure S8. Bond lengths (Å) on the bond path in P3.

Table S2. Bond lengths (Å) on the bond path in P1.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12
PBE	1.408	1.411	1.408	1.455	1.389	1.427	1.420	1.397	1.435	1.426	1.385	1.45
M06L	1.397	1.402	1.397	1.447	1.378	1.418	1.409	1.387	1.424	1.417	1.374	1.442
HSE06	1.392	1.407	1.391	1.452	1.373	1.423	1.407	1.387	1.422	1.422	1.369	1.447
B3LYP	1.395	1.412	1.395	1.459	1.376	1.429	1.411	1.390	1.426	1.428	1.371	1.454
PBE0	1.390	1.408	1.390	1.455	1.372	1.425	1.406	1.387	1.421	1.424	1.368	1.449
M06	1.387	1.409	1.387	1.453	1.370	1.424	1.404	1.386	1.419	1.423	1.366	1.448
M06-2X	1.382	1.418	1.382	1.463	1.365	1.433	1.403	1.387	1.418	1.433	1.362	1.458
OT-ωB97X	1.396	1.421	1.396	1.469	1.377	1.438	1.415	1.398	1.430	1.436	1.373	1.465
ωB97XD	1.381	1.418	1.381	1.466	1.363	1.435	1.403	1.389	1.417	1.434	1.360	1.462
LC-ωPBE	1.370	1.422	1.370	1.468	1.356	1.436	1.397	1.385	1.411	1.436	1.353	1.464
M06-HF	1.371	1.432	1.371	1.473	1.356	1.445	1.399	1.386	1.414	1.446	1.354	1.470
HF	1.359	1.433	1.359	1.474	1.344	1.445	1.393	1.380	1.406	1.444	1.341	1.471
PM6	1.378	1.433	1.378	1.447	1.362	1.447	1.413	1.387	1.430	1.452	1.358	1.449

Table S3. Bond lengths (Å) on the bond path in P2.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16	#17	#18	#19	#20
PBE	1.421	1.396	1.406	1.460	1.405	1.396	1.419	1.460	1.393	1.413	1.395	1.450	1.406	1.409	1.406	1.450	1.395	1.414	1.393	1.460
M06L	1.411	1.386	1.397	1.452	1.396	1.387	1.409	1.451	1.382	1.404	1.384	1.441	1.396	1.401	1.396	1.441	1.384	1.404	1.382	1.451
HSE06	1.408	1.387	1.395	1.456	1.394	1.387	1.407	1.457	1.379	1.410	1.380	1.447	1.390	1.406	1.390	1.447	1.380	1.410	1.378	1.458
B3LYP	1.412	1.391	1.398	1.462	1.397	1.392	1.411	1.463	1.380	1.415	1.382	1.453	1.393	1.410	1.393	1.453	1.382	1.415	1.380	1.464
PBE0	1.407	1.387	1.394	1.457	1.393	1.388	1.406	1.459	1.378	1.411	1.379	1.449	1.388	1.407	1.389	1.449	1.379	1.411	1.377	1.459
M06	1.406	1.386	1.392	1.456	1.391	1.387	1.405	1.457	1.375	1.410	1.377	1.448	1.386	1.408	1.386	1.448	1.377	1.411	1.374	1.458
M06-2X	1.405	1.389	1.393	1.466	1.392	1.390	1.404	1.467	1.372	1.418	1.374	1.457	1.381	1.417	1.381	1.457	1.374	1.419	1.371	1.467
OT-ωB97X	1.414	1.396	1.401	1.470	1.400	1.397	1.413	1.473	1.382	1.422	1.384	1.463	1.393	1.419	1.394	1.463	1.384	1.422	1.382	1.473
ωB97XD	1.404	1.389	1.392	1.467	1.391	1.390	1.403	1.470	1.371	1.419	1.373	1.461	1.380	1.417	1.380	1.461	1.373	1.419	1.371	1.470
LC-ωPBE	1.398	1.385	1.387	1.467	1.386	1.386	1.398	1.471	1.365	1.419	1.366	1.463	1.370	1.420	1.370	1.463	1.366	1.419	1.364	1.471
M06-HF	1.402	1.390	1.391	1.476	1.390	1.391	1.402	1.478	1.366	1.429	1.367	1.468	1.370	1.431	1.370	1.469	1.367	1.430	1.366	1.478
HF	1.396	1.383	1.385	1.470	1.384	1.384	1.395	1.477	1.351	1.429	1.353	1.469	1.359	1.431	1.359	1.469	1.353	1.429	1.351	1.477
PM6	1.403	1.404	1.387	1.469	1.387	1.405	1.401	1.454	1.365	1.441	1.367	1.448	1.378	1.433	1.378	1.448	1.367	1.441	1.365	1.454

Table S4. Bond lengths (Å) on the bond path in P3.

	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15	#16	#17	#18	#19	#20
PBE	1.420	1.396	1.405	1.461	1.405	1.397	1.418	1.462	1.389	1.424	1.398	1.461	1.404	1.415	1.404	1.461	1.398	1.424	1.390	1.462
M06L	1.410	1.387	1.397	1.452	1.396	1.387	1.408	1.453	1.379	1.414	1.387	1.452	1.393	1.406	1.393	1.452	1.387	1.414	1.379	1.453
HSE06	1.407	1.387	1.394	1.457	1.394	1.388	1.406	1.459	1.375	1.419	1.382	1.458	1.387	1.412	1.387	1.458	1.382	1.419	1.375	1.459
B3LYP	1.411	1.391	1.398	1.463	1.397	1.392	1.410	1.465	1.377	1.425	1.384	1.465	1.391	1.417	1.390	1.465	1.383	1.425	1.377	1.465
PBE0	1.407	1.388	1.394	1.458	1.393	1.389	1.406	1.461	1.374	1.420	1.382	1.459	1.386	1.413	1.386	1.460	1.381	1.420	1.375	1.461
M06	1.405	1.387	1.392	1.457	1.392	1.388	1.404	1.458	1.372	1.419	1.379	1.457	1.384	1.413	1.384	1.457	1.379	1.418	1.372	1.458
M06-2X	1.405	1.389	1.393	1.466	1.392	1.390	1.404	1.467	1.369	1.426	1.375	1.465	1.380	1.422	1.380	1.465	1.375	1.426	1.370	1.467
OT-ωB97X	1.412	1.396	1.400	1.471	1.399	1.397	1.411	1.474	1.378	1.431	1.385	1.473	1.390	1.424	1.390	1.473	1.384	1.431	1.379	1.474
ωB97XD	1.404	1.390	1.392	1.468	1.391	1.390	1.403	1.471	1.369	1.427	1.375	1.469	1.379	1.421	1.379	1.470	1.374	1.427	1.369	1.470
LC-ωPBE	1.398	1.386	1.387	1.468	1.387	1.386	1.398	1.472	1.363	1.426	1.368	1.470	1.369	1.425	1.368	1.470	1.367	1.426	1.363	1.472
M06-HF	1.402	1.390	1.391	1.477	1.391	1.391	1.401	1.479	1.364	1.436	1.368	1.475	1.370	1.435	1.369	1.475	1.367	1.436	1.364	1.479
HF	1.396	1.383	1.385	1.470	1.384	1.384	1.395	1.478	1.349	1.438	1.353	1.478	1.357	1.436	1.357	1.479	1.352	1.438	1.349	1.478
PM6	1.401	1.405	1.387	1.469	1.387	1.404	1.402	1.455	1.363	1.451	1.371	1.448	1.376	1.434	1.377	1.445	1.375	1.447	1.365	1.455

Effect of the method on the HOMO–LUMO gaps of the D–A copolymers P1–P3

The HOMO–LUMO gaps of the oligomers and the HOCO–LUCO gap of the polymers P1–P3 are presented in Tables S5–S7. The extrapolated gaps were obtained by presenting the HOMO–LUMO gaps as a function of 1/N, where N is the number of double bonds along the shortest path in the polymer backbone, and by plotting a 2nd or 3rd degree polynomial function on the data points. The values of N are multiples of 6, 10 and 10 for P1, P2, and P3, respectively (see Figures S4 and S5).

Table S5. HOMO–LUMO and HOCO–LUCO gaps (eV) of the P1 models.

	N = 6	N = 12	N = 18	N = 24	N = 30	N = 36	N = 42	N = 48	PBC
PBE	1.785	1.372	1.216	1.140	1.098	1.075	1.057	1.044	0.998
M06L	1.964	1.522	1.357	1.275	1.235	1.206	1.190	1.177	1.133
HSE06	2.616	2.091	1.894	1.807	1.759	1.729	1.712	1.699	1.620
B3LYP	3.019	2.495	2.301	2.209	2.163	2.135	2.116	2.103	2.013
PBE0	3.346	2.794	2.593	2.502	2.449	2.422	2.399	2.388	2.289
M06	3.383	2.856	2.659	2.571	2.519	2.500	2.468	2.463	2.373
M06-2X	5.033	4.413	4.217	4.099	4.059	4.041	4.022	4.011	3.925
OT-ωB97X	5.670	-	-	-	-	-	-	4.153	4.105
ωB97XD	6.535	5.914	5.727	5.641	5.582	5.555	5.551	5.532	5.466
LC-ωPBE	7.567	6.930	6.732	6.644	6.602	6.575	6.559	6.548	6.492
M06-HF	7.805	7.126	6.926	6.854	6.797	6.776	6.772	6.749	6.691
HF	8.624	7.977	7.781	7.698	7.655	7.631	7.616	7.605	7.566
PM6	6.410	6.032	5.975	5.937	5.934	5.912	5.911	5.903	-

Table S6. HOMO–LUMO and HOCO–LUCO gaps (eV) of the P2 models.

	N=10	N=20	N=30	N=40	PBC
PBE	1.613	1.384	1.310	1.278	1.218
M06L	1.761	1.506	1.426	1.384	1.330
HSE06	2.349	2.084	2.004	1.969	1.913
B3LYP	2.727	2.465	2.386	2.352	2.297
PBE0	3.062	2.785	2.704	2.668	2.614
M06	3.113	2.852	2.769	2.735	2.679
M06-2X	4.741	4.443	4.361	4.322	4.272
OT-ωB97X	5.375	-	-	4.711	4.658
ωB97XD	6.235	5.972	5.873	5.839	5.792
LC-ωPBE	7.307	7.037	6.936	6.913	6.838
M06-HF	7.550	7.289	7.189	7.173	7.105
HF	8.182	7.921	7.806	7.787	7.681
PM6	6.833	6.736	6.683	6.678	-

Table S7. HOMO–LUMO and HOCO–LUCO gaps (eV) of the P3 models.

	N=10	N=20	N=30	N=40	PBC
PBE	1.796	1.591	1.526	1.500	1.457
M06L	1.946	1.732	1.662	1.631	1.587
HSE06	2.635	2.385	2.315	2.287	2.242
B3LYP	3.030	2.783	2.716	2.689	2.647
PBE0	3.373	3.109	3.038	3.009	2.964
M06	3.373	3.132	3.055	3.031	2.986
M06-2X	5.075	4.785	4.710	4.681	4.635
OT-ωB97X	5.689	-	-	5.361	5.329
ωB97XD	6.618	6.323	6.255	6.231	6.207
LC-ωPBE	7.742	7.432	7.365	7.338	7.300
M06-HF	7.948	7.631	7.566	7.535	7.495
HF	8.718	8.387	8.327	8.304	8.271
PM6	6.972	6.888	6.863	6.854	-

Effect of the method on the first electronic excitation

The first excitation energy of the oligomers and polymers P1–P3 are presented in Tables S8–S10. The extrapolated excitation energies were obtained by presenting the oligomer excitation energies as a function of 1/N, where N is the number of double bonds along the shortest path in the polymer backbone, and plotting a 2nd, 3rd, or 4th degree polynomial function on the data points. The values of N are multiples of 6, 10, and 10 for P1, P2, and P3, respectively (see Figures S4 and S5).

Table S8. First excitation energy (eV) of the P1 models.

	N = 6	N = 12	N = 18	N = 24	N = 30	N = 36	N = 42	N = 48
PBE	1.972	1.616	1.392	1.261	1.182	1.135	1.102	1.078
M06L	2.151	1.759	1.522	1.390	1.313	1.263	1.232	1.210
HSE06	2.650	2.176	1.942	1.824	1.759	1.719	1.696	1.679
B3LYP	2.655	2.204	2.008	1.909	1.860	1.830	1.810	1.796
PBE0	2.833	2.349	2.155	2.064	2.012	1.985	1.962	1.951
M06	2.791	2.314	2.127	2.042	1.991	1.971	1.941	1.936
M06-2X	3.509	2.937	2.777	2.666	2.648	2.634	2.617	2.607
OT-ωB97X	-	-	-	-	-	-	-	2.261
ωB97XD	3.663	3.088	2.951	2.851	2.841	2.820	2.817	2.802
LC-ωPBE	4.111	3.539	3.395	3.331	3.299	3.278	3.265	3.256
M06-HF	4.242	3.673	3.529	3.482	3.438	3.423	3.419	3.401
HF	4.476	3.860	3.722	3.662	3.630	3.611	3.599	3.591

Table S9. First excitation energy (eV) of the P2 models.

	N=10	N=20	N=30	N=40
PBE	1.971	1.511	1.388	1.317
M06L	2.099	1.633	1.502	1.434
HSE06	2.471	2.107	1.997	1.949
B3LYP	2.442	2.157	2.068	2.030
PBE0	2.601	2.320	2.234	2.197
M06	2.531	2.278	2.194	2.159
M06-2X	3.120	2.882	2.818	2.786
OT-ωB97X	-	-	-	2.509
ωB97XD	3.205	3.020	2.953	2.926
LC-ωPBE	3.647	3.464	3.399	3.382
M06-HF	3.816	3.641	3.583	3.570
HF	3.891	3.710	3.640	3.622

Table S10. First excitation energy (eV) of the P3 models.

	N=10	N=20	N=30	N=40
PBE	2.007	1.678	1.579	1.534
M06L	2.170	1.819	1.714	1.665
HSE06	2.636	2.356	2.273	2.240
B3LYP	2.627	2.404	2.340	2.314
PBE0	2.809	2.577	2.512	2.485
M06	2.716	2.508	2.437	2.415
M06-2X	3.402	3.188	3.131	3.107
OT-ωB97X	-	-	-	2.930
ωB97XD	3.555	3.366	3.316	3.297
LC-ωPBE	4.065	3.864	3.810	3.788
M06-HF	4.177	3.986	3.940	3.915
HF	4.447	4.175	4.120	4.097

Effect of the method on the HOMO and LUMO and their electron densities

The procedure to extract and calculate the electron density distribution for periodic Gaussian calculations is shown (C squared population analysis, CSPA).[1] Although the procedure is available in many programs used for analyzing the results the periodic boundary conditions might cause problems.

1. The Gaussian formchk utility was used to create the formatted checkpoint file (.fchk) from the checkpoint (.chk) file.

2. (Alpha) MO coefficients were extracted from the .fchk file.

3. The coefficients for the orbitals of interest (here the highest occupied and the lowest unoccupied orbitals) were squared to obtain the electron density.

4. The electron density was assigned to the donor and acceptor units by summing the electron density of the atoms in the units mentioned.

5. The amount of the electron density in a donor/acceptor was compared to the total electron density of the molecular orbital to see its total contribution.

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1 P. Ros, G. C. A. Schuit, *Theo. Chim Acta.*, 1966, **4**, 1–12.