

Electronic Supplementary Information: Rational Design of D–A₁–D–A₂ Conjugated Polymers with Superior Spectral Coverage

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Table S1. Average out-of-plane dihedral angles of PTQTI, PBTDP, and PBBTDPP, as calculated with ω B97XD, and with PBE0 with and without a polarizable continuum medium (PCM) chloroform solvent. The ω B97XD structures are systematically less planar than PBE0, attributed to a larger amount of exact exchange with this functional as a result of a large LC parameter ω . The fact that the difference in planarity in PTQTI is similar to the other two polymers indicates that the dispersion interaction that could potentially be of significance for PTQTI (interactions between the side groups on isoindigo and alkoxyphenyl-quinoxaline) is not what mainly determines the planarity, which is the most important structural property for electronic and optical properties in conjugated systems. The addition of the PCM solvent does not noticeably affect the planarity.

Method	PTQTI	PBTDP	PBBTDPP
PBE0/6-31G(d,p)	10.5	1.0	0.0
PBE0/6-31G(d,p)+PCM(CHCl ₃)	10.4	1.0	0.4
ω B97XD/6-31G(d,p)	18.4	12.4	7.9

Table S2. Calculated HOMO (H), LUMO (L), and LUMO+1 (L+1) energies of all D–A₁–D–A₂ polymers, as monomers and as infinite polymers by linear extrapolation to 1/n=0 after plotting mono- and dimer orbital energies vs. 1/n. Note that the longer repeating unit resulting from using a 3T donor inevitably stabilizes monomer LUMO and destabilizes HOMO, compared to T donor monomers. The planarity of the polymers is presented as the average out-of-plane dihedral angles of dimers.

Polymer	H _{mono} [eV]	L _{mono} [eV]	L+1 _{mono} [eV]	H _{poly} [eV]	L _{poly} [eV]	Out-of-plane [°]
PTQTI	-5.19	-2.62	-2.17	-4.85	-2.89	10.5
PBTDDPP	-5.00	-2.8	-2.37	-4.75	-3.22	1.0
PBBTDPP	-4.93	-3.56	-2.49	-4.58	-3.82	0.0
PTPhQBTz	-5.13	-2.11	-1.6	-4.49	-2.59	7.7
PTPzQPhQ	-5.23	-2.78	-2.08	-4.42	-3.08	12.8
PTBTBTz	-5.34	-2.45	-1.83	-4.78	-3.01	0.7
PTIIBTz	-5.27	-2.68	-1.92	-4.98	-2.93	10.0
PTPzQBTz	-5.21	-2.87	-1.79	-4.50	-3.23	5.7
P3TPhQBTz	-4.88	-2.32	-2.05	-4.65	-2.62	9.0
P3TPzQPhQ	-4.85	-2.98	-2.36	-4.57	-3.17	10.2
P3TBTBTz	-5.00	-2.64	-2.19	-4.82	-2.85	0.0
P3TIIBTz	-5.03	-2.76	-2.21	-4.93	-2.88	13.0
P3TPzQBTz	-4.91	-3.02	-2.15	-4.62	-3.19	7.1
P3TQTIF	-5.03	-2.75	-2.36	-4.94	-2.85	18.0
PTIIBTzF	-5.37	-2.69	-2.01	-5.06	-2.96	10.0

Table S3. List of electronic transitions with wavelengths and oscillator strengths of PTQTI, PBTDDPP, and PBBTDPP as calculated with TD-PBE0/6-31G(d,p)//PBE0/6-31G(d,p), with and without a PCM-CHCl₃ solvent. The addition of the implicit solvent strengthens the transitions and corresponding absorption peaks, and also slightly red-shifts the transitions in a systematic fashion. The overall absorption remains however mostly unchanged.

PTQTI							
Gas Phase				PCM (chloroform)			
Monomer		Dimer		Monomer		Dimer	
λ [nm]	f	λ [nm]	f	λ [nm]	f	λ [nm]	f
582.43	1.0325	678.98	2.9698	610.49	1.1967	706.56	3.1285
498.74	0.0036	589.00	0.0266	510.22	0.0106	616.74	0.0878
494.13	0.0866	560.93	0.0042	497.55	0.1647	573.69	0.0119
467.93	0.0613	526.92	0.1415	476.08	0.0235	537.37	0.1340
401.56	0.0863	520.57	0.0129	411.87	0.0295	520.34	0.0078
391.19	0.0625	503.81	0.0794	407.01	0.1483	509.78	0.0406
389.20	0.0207	500.95	0.0049	392.77	0.0517	507.83	0.0630
379.18	0.0108	497.48	0.0020				
369.22	0.0712	482.84	0.0258				
367.31	0.0176	475.99	0.1479				

364.59	0.0163	456.39	0.0075				
361.88	0.0078	441.26	0.0668				
354.07	0.1058	439.29	0.0166				
346.98	0.2427	430.84	0.0404				
344.24	0.1405	408.21	0.0080				
341.47	0.1514	403.79	0.0710				
337.05	0.0251	399.73	0.0351				
334.33	0.0784	397.81	0.0476				
328.55	0.0716	397.44	0.0951				
321.55	0.0114	394.78	0.0740				
319.72	0.0008	392.84	0.0051				
315.13	0.0763	389.68	0.0349				
307.73	0.0015	388.29	0.0034				
303.79	0.0081	383.04	0.0035				
299.84	0.0397	380.61	0.0420				
297.43	0.0244	377.35	0.0362				
293.77	0.0169	376.32	0.1064				
		372.85	0.0640				
		371.36	0.0202				
		370.83	0.0164				
		369.42	0.0077				
		367.56	0.0034				
		366.48	0.0044				
		364.94	0.0562				
		362.94	0.0642				
		359.22	0.0008				
		359.09	0.292				
		356.35	0.0523				
		355.23	0.0375				
		354.46	0.0613				
		352.97	0.0741				
		351.44	0.0021				
		350.33	0.0738				
		348.14	0.0134				
		346.83	0.0697				
		346.64	0.0198				
		345.43	0.1661				
		343.56	0.0164				
		342.59	0.0370				
		341.07	0.1146				
		338.65	0.0173				
		338.24	0.0264				
		337.10	0.0171				
		336.88	0.0977				
		336.70	0.0041				
		332.06	0.0117				
		331.22	0.0159				
		329.62	0.0067				
		326.64	0.0095				

		325.54	0.0298				
		325.25	0.0033				
		323.91	0.0208				
		323.20	0.0048				
		322.46	0.0040				
		321.40	0.0145				
		320.37	0.0133				
		319.34	0.0543				
		317.30	0.0210				
		315.36	0.0049				
		314.70	0.0061				

PBTDPP							
Gas Phase				PCM (chloroform)			
Monomer		Dimer		Monomer		Dimer	
λ [nm]	f	λ [nm]	f	λ [nm]	f	λ [nm]	f
659.96	1.1003	814.88	2.7899	668.94	1.6031	819.12	3.2717
538.26	0.6243	685.74	0.1686	542.51	0.2768	682.78	0.4404
499.38	0.1144	676.11	0.2781	505.04	0.1967	663.6	0.1411
427.44	0.0117	583.48	0.2165	430.52	0.0028	582.89	0.3840
395.42	0.0643	572.92	0.3515	394.71	0.0557	572.89	0.2375
378.79	0.1421	561.12	0.5187	380.65	0.1417	556.76	0.1832
369.85	0.0085	540.94	0.0043	372.03	0.0062	543.70	0.0258
345.20	0.0170	520.18	0.3110			521.49	0.1080
336.02	0.1834	503.02	0.1226			507.62	0.3329
332.04	0.0027	495.50	0.0352			487.90	0.0100
		486.15	0.0004				
		450.01	0.0062				
		437.26	0.0130				
		427.99	0.0039				
		425.06	0.0074				
		415.20	0.0315				
		404.04	0.0523				
		394.12	0.0145				
		392.19	0.1955				
		384.93	0.0942				
		379.63	0.0017				
		377.19	0.0002				
		373.74	0.0585				
		369.81	0.0445				
		366.88	0.006				
		362.97	0.0456				
		359.57	0.1401				
		346.52	0.0188				
		345.54	0.0808				
		340.84	0.2130				

PBBTDPP							
Gas Phase				PCM (chloroform)			
Monomer		Dimer		Monomer		Dimer	
λ [nm]	f	λ [nm]	f	λ [nm]	f	λ [nm]	f
1070.31	0.6611	1422.81	2.4606	1082.12	0.8871	1441.69	2.7689
772.84	0.0918	1195.25	0.0387	752.20	0.0707	1160.78	0.0779
573.88	1.0155	1042.29	0.0004	600.03	1.0196	1033.13	0.0032
497.62	0.0053	929.79	0.0709	491.86	0.0057	897.21	0.0979
470.39	0.0137	835.74	0.0060	471.73	0.0391	817.55	0.0032
461.56	0.0214	780.63	0.1688	455.45	0.0046	756.77	0.1378
431.64	0.0006	733.96	0.1067	421.69	0.0005	709.37	0.1472
428.75	0.0012	658.14	0.0660				
406.68	0.0091	646.99	1.4585				
398.24	0.1611	607.86	0.0987				
377.91	0.0868	554.50	0.0037				
367.69	0.0012	535.60	0.3472				
364.42	0	521.77	0.0015				
354.36	0.0017	500.29	0.0033				
352.52	0.0709	482.66	0.0068				
351.53	0.0081	469.37	0.0007				
347.13	0.2427	467.76	0.0268				
341.41	0.0014	460.07	0.0273				
331.87	0.0105	452.15	0.0002				
330.44	0.0274	449.38	0.0055				
326.86	0	446.00	0.0382				
322.74	0	442.87	0.0099				
321.72	0.0001	436.81	0.0007				
321.30	0.2357	435.35	0.0005				
314.17	0	434.83	0.0023				
		428.92	0.0017				
		427.05	0.0033				
		425.85	0.0724				
		415.33	0.0095				
		415.10	0.0007				
		404.21	0.3671				
		400.33	0.0017				
		392.65	0.0134				
		391.02	0.0203				
		384.32	0.0029				
		379.93	0.0031				
		377.86	0.0162				
		377.26	0.0002				
		376.67	0.0003				
		375.16	0.0011				
		372.97	0				
		371.94	0.3058				
		371.31	0				
		368.10	0.0059				
		365.84	0.0083				

		363.84	0.0030				
		360.78	0.0050				
		360.23	0.1339				
		359.11	0.0398				
		357.01	0				
		354.14	0				
		353.46	0.0008				
		352.90	0.0620				
		351.19	0.0146				
		349.81	0.0101				

Table S4. Calculated monomer LUMO and LUMO+1 energies of the ten computational D–A₁–D–A₂ polymers compared to the difference in single molecule acceptor energy ($\Delta E_{\text{LUMO,A}}$). Sorted by falling $\Delta E_{\text{LUMO,A}}$.

	PnTPzQBTz	PnTIIBTz	PnTBTBTz	PnTPzQPhQ	PnTPhQBTz
A ₁	PzQ	II	BT	PzQ	PhQ
A ₂	BTz	BTz	BTz	PhQ	BTz
E _{LUMO} (n=1)	-2.87	-2.68	-2.45	-2.78	-2.11
E _{LUMO+1} (n=1)	-1.79	-1.92	-1.83	-2.08	-1.60
E _{LUMO} (n=3)	-3.02	-2.75	-2.63	-2.98	-2.32
E _{LUMO+1} (n=3)	-2.15	-2.21	-2.19	-2.36	-2.05
$\Delta E_{\text{LUMO(A)}}$	1.70	1.55	1.17	0.97	0.73

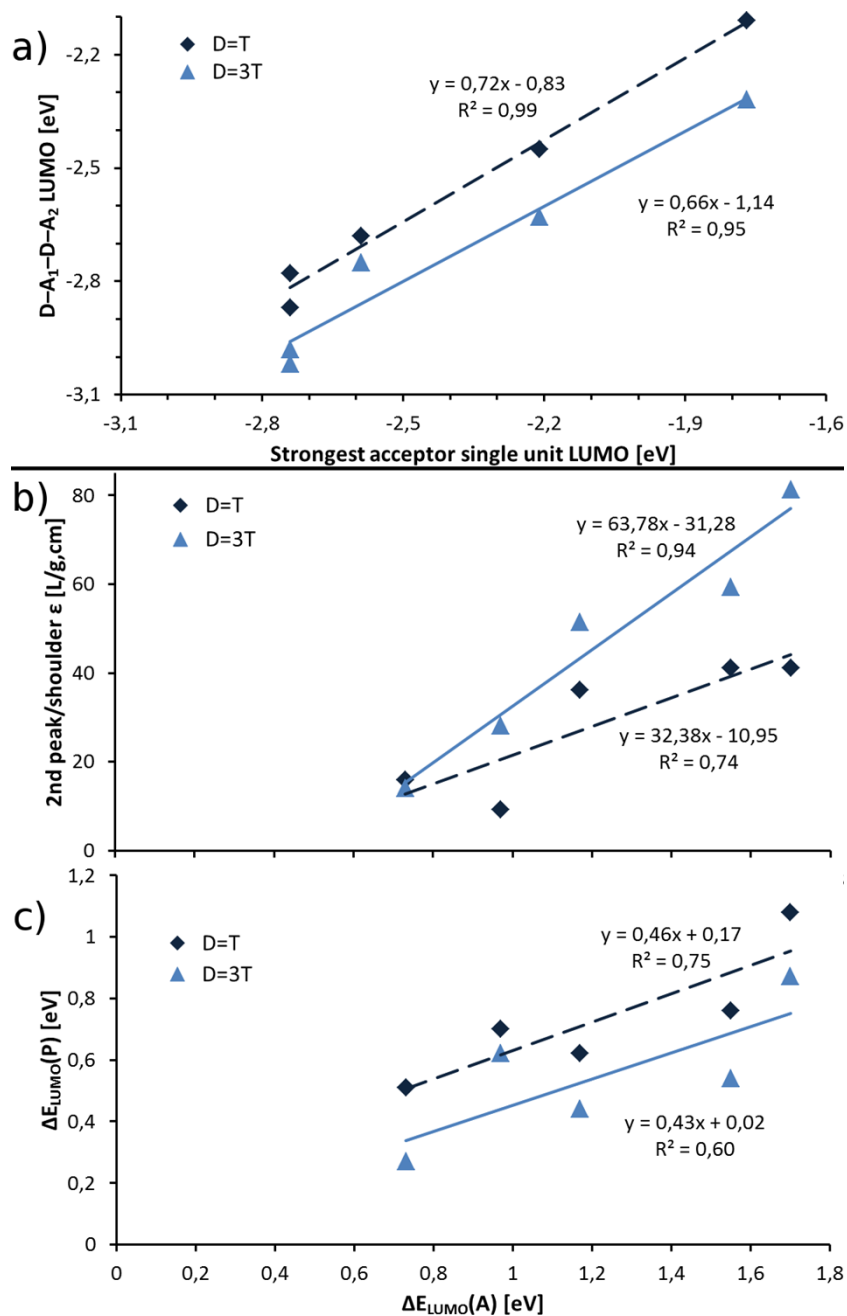


Figure S1. Calculated D-A₁-D-A₂ comonomer LUMO energy vs. LUMO energy of the strongest acceptor (a). Calculated maximum absorption coefficient of the second absorption feature vs. difference in LUMO energy between the two acceptor units (b). Difference between LUMO and LUMO+1 in the D-A₁-D-A₂ comonomers vs. difference in LUMO energy between the two acceptor units (c).

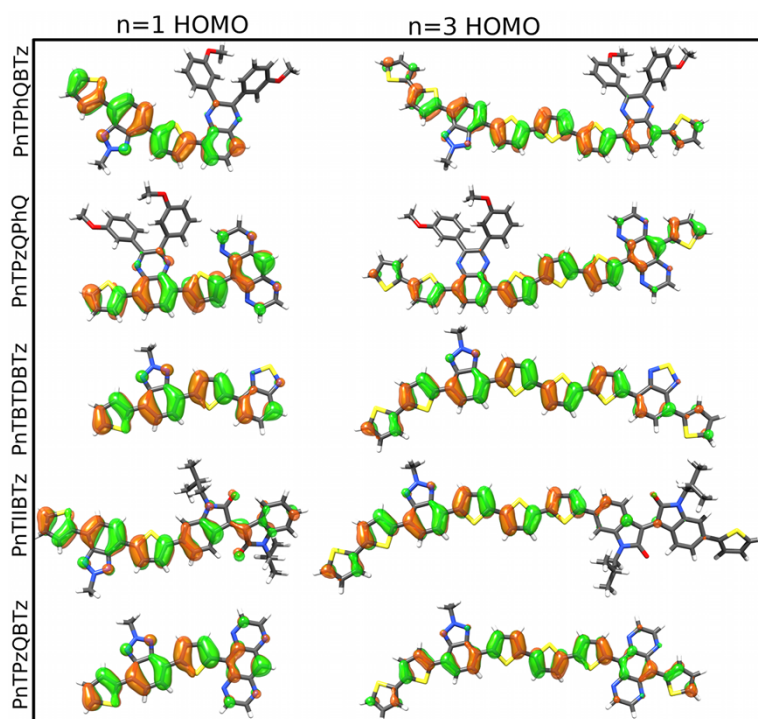


Figure S2. HOMOs of the 10 computational D–A₁–D–A₂ copolymers. All are well delocalized over the backbones.

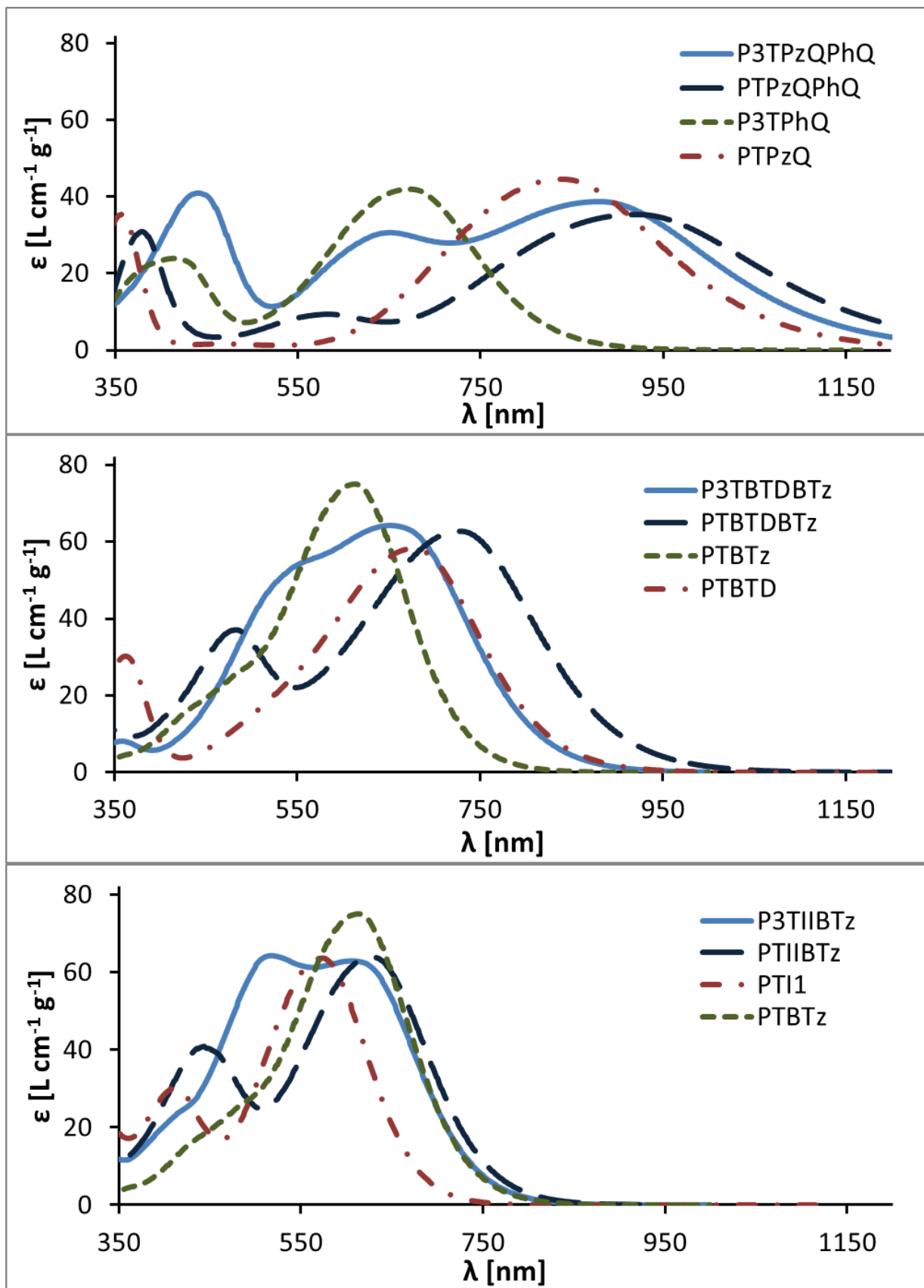


Figure S3. Spectra of PnTPzQPhQ, PnTBTBTz, and PnTIIBTz compared to their corresponding D–A polymer spectra. PTI1 exhibits a shorter wavelength peak than PTBTz, even though isoindigo has a lower LUMO than benzotriazole. This is rationalized from the extremely planar structure of PTBTz, whereas PTI1 has a considerable dihedral angle between T and II, weakening the conjugation.

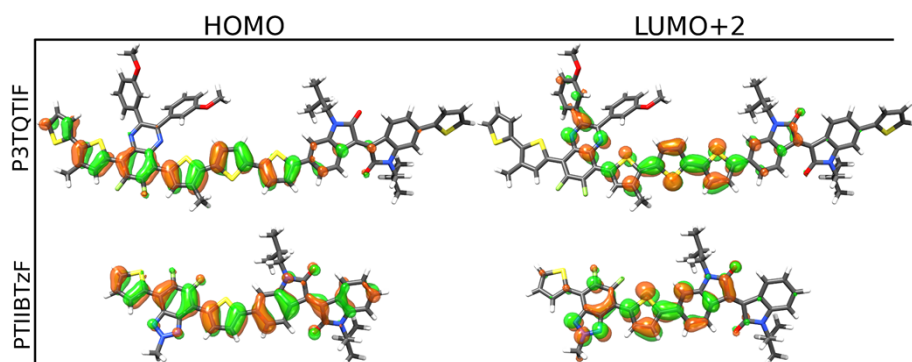
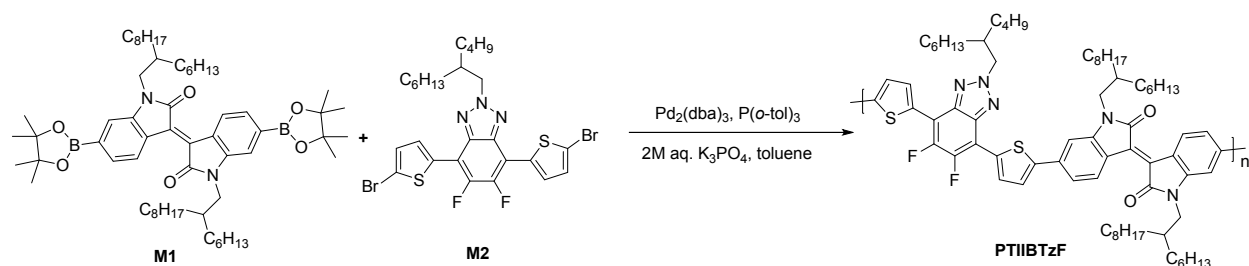


Figure S4. The HOMO and LUMO+2 orbitals of P3TQTIF and PTIIBTzF. All show some delocalization, but LUMO+2 are for both polymers strongest on the donors.

Synthesis of PTIIBTzF



Scheme 1. Synthetic route of the polymer **PTIIBTzF**.

All reagents and starting materials were purchased from commercial sources and used without further purification, unless otherwise noted. The monomers (*E*)-1,1'-bis(2-hexyldecyl)-6,6'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[3,3'-biindolinylidene]-2,2'-dione (**M1**)¹ and 4,7-bis(5-bromothiophen-2-yl)-2-(2-butyloctyl)-5,6-difluoro-2H-benzo[d][1,2,3]triazole (**M2**)² were prepared according to the literature methods.

In a dry 25 mL flask, **M1** (193 mg, 0.2 mmol), **M2** (129 mg, 0.2 mmol), Aliquat 336 (3 drops), tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] (3.0 mg), tri(*o*-tolyl)phosphine [P(*o*-Tol)₃] (6.0 mg) and K₃PO₄ (500 mg) were dissolved in a mixture of degassed toluene (6 mL) and deionized water (1 mL). The mixture was vigorously stirred at 100 °C for 18 h under nitrogen.

After that, it was cooled down and poured into acetone. The polymer was collected by filtration through 0.45 μm Teflon filter and Soxhlet-extracted first with diethyl ether, and then with chloroform. The chloroform solution was passed a short column and precipitated into acetone. Finally, the polymer was collected by filtration using a 0.45 μm Teflon filter and dried under vacuum at 40 °C overnight (100 mg, 42%). $M_n = 26.4$ kDa, PDI = 1.9.

Supplementary information references

- 1 W. Sun, Z. Ma, D. Dang, W. Zhu, M. R. Andersson, F. Zhang and E. Wang, *J. Mater. Chem. A*, 2013, **1**, 11141–11144.
- 2 S. C. Price, A. C. Stuart, L. Yang, H. Zhou and W. You, *J. Am. Chem. Soc.*, 2011, **133**, 4625–4631.