Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2014

Supporting Information:

Assessment of light-harvesting capability of conjugated polymers

Svante Hedström,[†] *Patrik Henriksson,*[‡] *Ergang Wang,*[‡] *Mats R. Andersson,*[‡] *and Petter Persson**[†]

[†]Division of Theoretical Chemistry, Lund University. P.O.B 124, S-221 00 Lund, Sweden.

[‡]Department of Chemical and Biological Engineering/Polymer Technology, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Optimized monomers

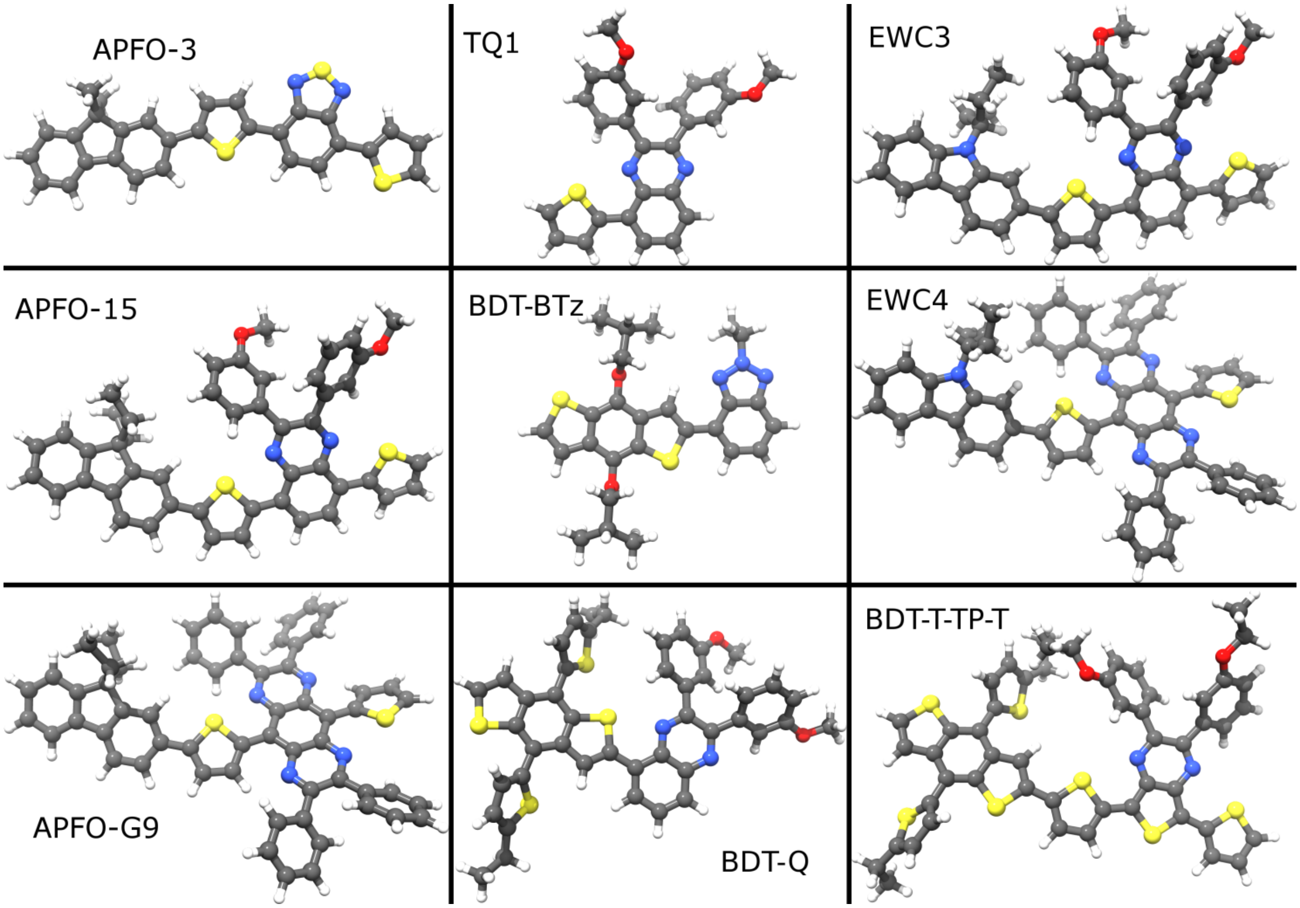

Figure S1. Calculated minimum energy conformation of monomers, optimized with PBE0/6-31G(d,p).

Square wave voltammetry measurements

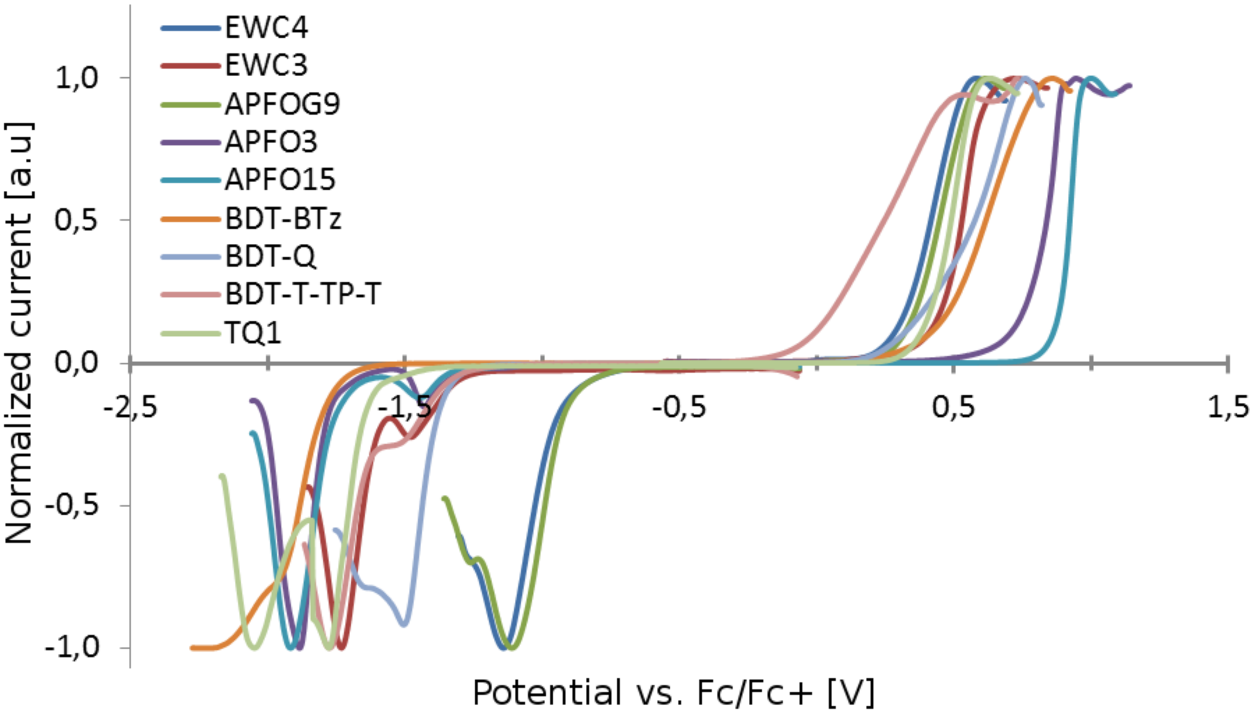

Figure S2. SWV measurement plots vs. Ferrocene/Ferrocenium$^+$ of all polymers in the study.

Absorption strength and energies

Table S1. Energy of maximum absorption and absorption strength per weight for all polymers. Experimental and as calculated, extrapolated to experimental molecular weights.

	BDT-T-TP-T	EWC4	APFOG9	TQ1	BDT-Q	APFO3	BDT-BTz	APFO15	EWC3
$E_{abs.exp}$/eV	1.77	1.78	1.78	2.04	2.16	2.24	2.32	2.33	2.33
$E_{abs.calc}$/eV	1.40	1.41	1.46	1.91	1.81	1.92	1.97	1.95	2.02
$F_{M.exp}$/kg^{-1}	0.45	0.38	0.48	0.60	0.37	1.18	1.06	0.73	0.61
$F_{M.calc}$/kg^{-1}	1.00	0.71	0.68	0.87	0.62	1.96	1.86	0.90	0.90

Size dependence of oscillator strength per weight, F_M

The oscillator strength or f-value, increases linearly with number of units n, according to Equation 3 for all polymers.[1]

$$\sum_{1st\ peak} f = an + b \ \rightarrow \ \frac{\sum_{1st\ peak} f}{n} \equiv F_n = a + \frac{b}{n} \tag{3}$$

Equation 3, where *a* and *b* are polymer-specific constants, shows that the first peak absorption strength per repeating unit is linear when plotted against 1/n. By further dividing by the molecular mass of the repeating unit (M_{rep}), we obtain Equation 4, where a_2 and b_2 are new polymer-specific constants and the total molecular mass $M = M_{rep} \times n$. Thus F_M is linear when plotted vs 1/n.

$$\frac{\sum_{1st\ peak} f}{M} \equiv F_M = \frac{a}{M_{rep}} + \frac{b}{M_{rep} \times n} = a_2 + b_2 \times \frac{1}{n} \tag{4}$$

The F_M values depend on the number of repeating units, but they converge for longer polymers as 1/n. For TQ1, experimental absorption measurements have been done for five different batches with different molecular weights, and the resulting oscillator strengths per weight is plotted in Figure S3A. They are there compared to calculated ones, obtained through the extrapolation from Figure 6 to the corresponding experimental M, with the added empirical correction. The experimental results show a linear behavior just like the calculations, but exhibit a much slower convergence. The main reason for this is assigned to the experimental overestimation of molecular weights. By dividing the SEC estimated molecular weights by 2, the experimental slope in Figure S3B is in better agreement with calculations. It is possible that the F_M-values for the other polymers investigated in this study are not fully converged due to their limited molecular weights as reported in Table 1.

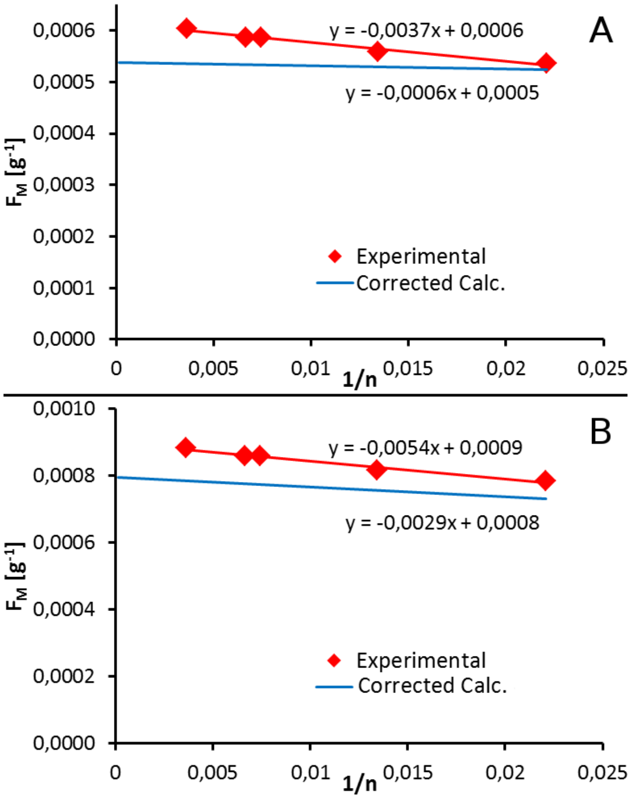

Figure S3. A: TQ1 experimental and calculated convergence of absorption strength per weight *vs*. inverse number of repeating units. Calculated values are obtained from the linear extrapolation in Figure 6 and experimental according to Equation 5. The linear fit equations reveal a considerably slower convergence for the experimental results, explained by the SEC overestimation of molecular weights. B: as A but with the SEC molecular weight estimations halved. The slopes are now similar for calculation and experiment.

Synthesis of BDT-BTz

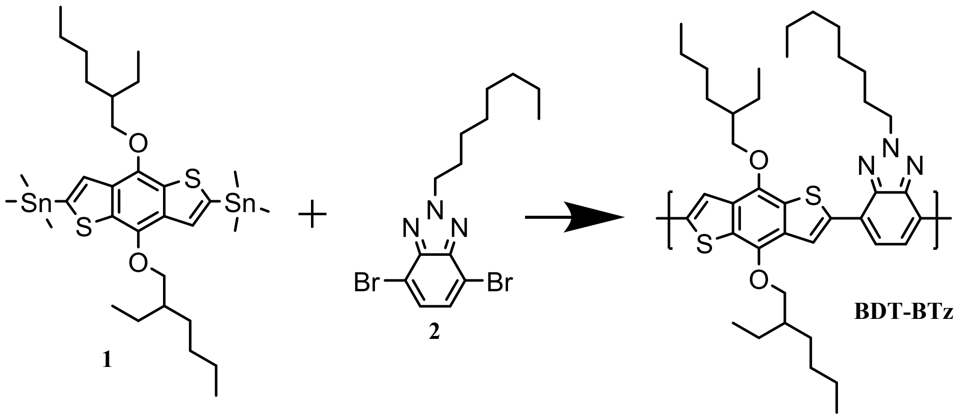

Figure S4. Synthesis steps of BDT-BTz.

Monomer **1** was purchased from Solarmer Materials Inc. and used as received. Monomer **2,** was synthesized according to literature.[2] Monomer **1** (0.79 g, 1.03 mmol), monomer **2** (0.4 g, 1.03 mmol), $Pd_2(dba)_3$ (38 mg) and $P(o\text{-}Tol)_3$ (100 mg) were added to a dry 50 mL flask and dissolved in degassed toluene (20 mL). The reaction mixture was stirred vigorously whilst refluxed for 5 h. The polymer was precipitated in stirring methanol and collected via filtration through 0.45 μm Teflon filter and washed twice with methanol. The polymer was then dissolved in chloroform (300 mL) and stirred at 60 ˚C overnight with a solution of sodium diethyldithiocarbamate trihydrate (10 wt%, 100 mL). The organic phase was extracted and washed twice with deionized water, concentrated via rotary evaporation and precipitated in methanol. The polymer was recovered via filtration through 0.45 μm Teflon filter and purified by Soxhlet extraction with in the following order; methanol, acetone, hexane and chloroform. The chloroform fraction was concentrated via rotary evaporation and poured into methanol and the polymer was collected after filtration through 0.45 μm Teflon filter and dried in vacuum oven (40 ˚C) overnight (549 mg, 75%).

Synthesis of BDT-Q

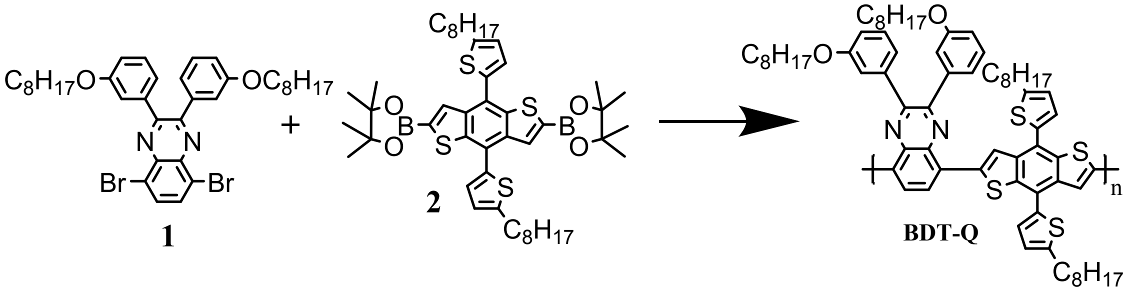

Figure S5. Synthesis steps of BDT-Q.

Monomer **1**, 5,8-dibromo-2,3-bis(3-(octyloxy)phenyl)quinoxaline was purchased from Solarmer Materials Inc. and used as received. Synthesis of monomer **2**, 2,2'-(4,8-bis(5-octylthiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) is described in the synthesis procedure for BDT-T-TP-T. Monomer 1 (377 mg, 0.54 mmol), monomer **2** (450 mg, 0.54 mmol), $Pd_2(dba)_3$ (20 mg) and $P(o\text{-}Tol)_3$ (53 mg) were added to a dry 50 mL flask and dissolved in dry THF (20 mL). The reaction was brought to reflux and after 15 minutes tetraethylammonium hydroxide solution (20 wt% in water (3 mL, 4.05 mmol) was added and the reaction was allowed to run for an additional 48 h. The polymer was poured into methanol and recovered by filtration through a 0.45 μm Teflon filter and washed twice with methanol. The polymer was dissolved in chloroform (200 mL) and stirred vigorously with a solution of sodium diethyldithiocarbamate trihydrate in deionized water (10 wt%, 100 mL) at 60 ˚C overnight. The organic phase was washed three times with water and concentrated by rotary evaporation. It was then precipitated in methanol and collected by filtration through a 0.45 μm Teflon filter. The polymer was further purified by Soxhlet extraction with the following solvents in the given order; methanol, acetone, hexane and chloroform. The chloroform fraction was concentrated by rotary evaporation and poured into methanol. The polymer was finally recovered by filtration through a 0.45 μm Teflon filter and dried in a vacuum oven (40 ˚C) overnight (440 mg, 73%).

Synthesis of BDT-T-TP-T

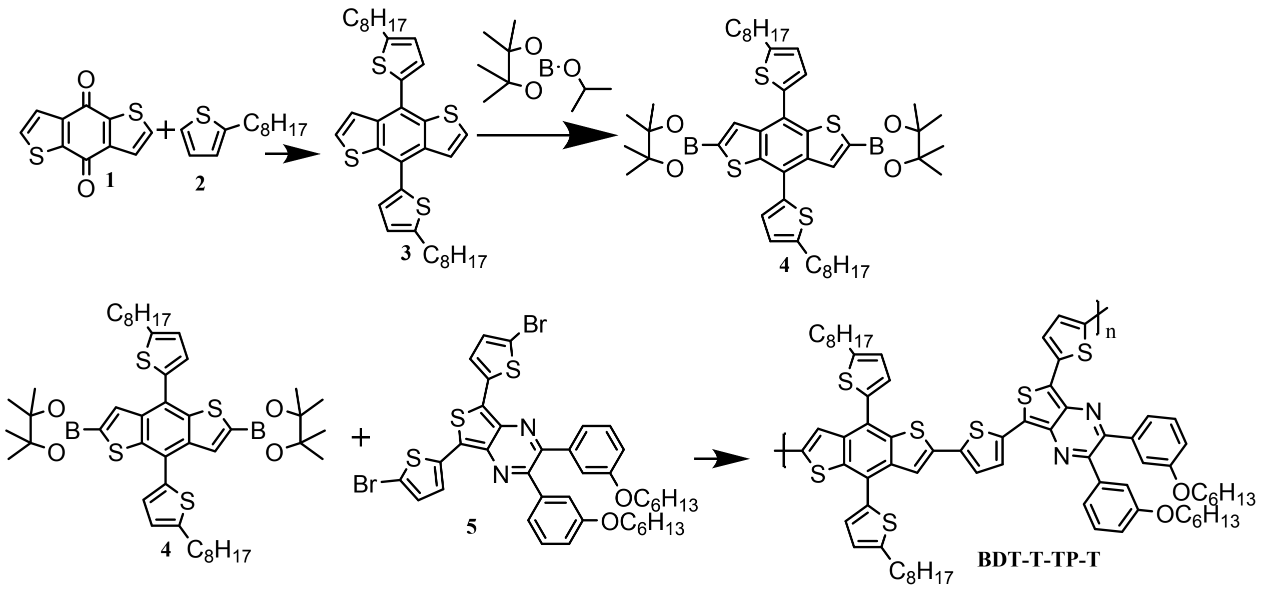

Figure S6. Synthesis steps of BDT-T-TP-T.

Compound **1**, 4,8-Dihydrobenzo[1,2-b:4,5-b’]dithiophene-4,8-dione was synthesized according to literature.[3]

To a dry 500 mL flask, 2-octyl thiophene (11 g, 56.3 mmol) was added and dissolved in dry THF (100 mL) and put in an ice bath. N-Butyllithium (25 mL, 60 mmol) was added drop wise to the reaction mixture and then the temperature was increased to 50 ˚C and stirred for 2 h. Compound **1** (3.1 g, 14 mmol) was dissolved in dry THF (70 mL) and added to the reaction mixture which was allowed to stir for 1 h. The temperature was lowered to ambient and $SnCl_2$ (21.3 g, 112.6 mmol) dissolved in 10% HCl was added and the mixture was stirred vigorously for 1.5 h and then poured over stirring water ice. The organic phase was extracted three times with diethyl ether and concentrated via rotary evaporation. The resulting compound was purified via column chromatography with petroleum ether and a final step of recrystallization from petroleum ether yielded compound **3**, 4,8-bis(5-octylthiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene (3.83 g, 47%) as yellow crystals.

Compound **3**, 4,8-bis(5-octylthiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene (2 g, 3.46 mmol) was added to a dry 50 mL flask and dry THF (40 mL) was added and the temperature was increased to 50 ˚C, then N-Butyllithium (2.9 mL, 7.23 mmol) was added drop wise and the reaction mixture was stirred vigorously for 2 h. The temperature was the lowered to ambient and 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.48 mg, 7.96 mmol) was added and the reaction was stirred for 1 h. The reaction mixture was then poured into 200 mL of cool deionized water and extracted by ether three times. The organic layer was washed by water two times and then dried by anhydrous MgSO4. After removing the solvent under vacuum, the residue was purified via column chromatography with petroleum ether/ethyl acetate (9:1) and yielded Compound **4**, 2,2'-(4,8-bis(5-octylthiophene-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (2.6 g, 90%).

Compound **5**, 2,3-bis(3-(hexyloxy)phenyl)-5,7-bis(5-methylthiophene-2-yl)thieno[3,4-b]pyrazine was synthesized according to literature.[4]

In a 25 mL dry flask, compound **4** (215 mg, 0.26 mmol), compound **5** (195 mg, 0.26 mmol), $Pd_2(dba)_3$ (26 mg) and $P(o\text{-Tol})_3$ (10 mg) were dissolved in degassed toluene (12 mL). The reaction mixture was heated to reflux. After 30 min, tetraethylammonium hydroxide solution (20 wt% in water (3 mL, 4.05 mmol) was added and the reaction was allowed to run for 48 h. The polymer was precipitated into stirring methanol and collected by filtration through 0.45 µm Teflon filter. The polymer was washed twice with methanol and then dissolved in chloroform (200 mL) and stirred gently together with a solution of sodium diethyldithiocarbamate trihydrate (5 wt%, 200 mL) overnight at 60 ˚C. The organic phase was separated and washed three times with deionized water, concentrated via rotary evaporation and poured into methanol. The polymer was then recovered by filtration through 0.45 µm Teflon filter and further purified via Soxhlet extraction with in the following order; methanol, acetone, hexane and chloroform. The chloroform fraction was concentrated via rotary evaporation and poured into methanol and the polymer was collected after filtration through 0.45 µm Teflon filter and dried in vacuum oven (40 ˚C) overnight (124 mg, 38%) .

Synthesis of EWC4

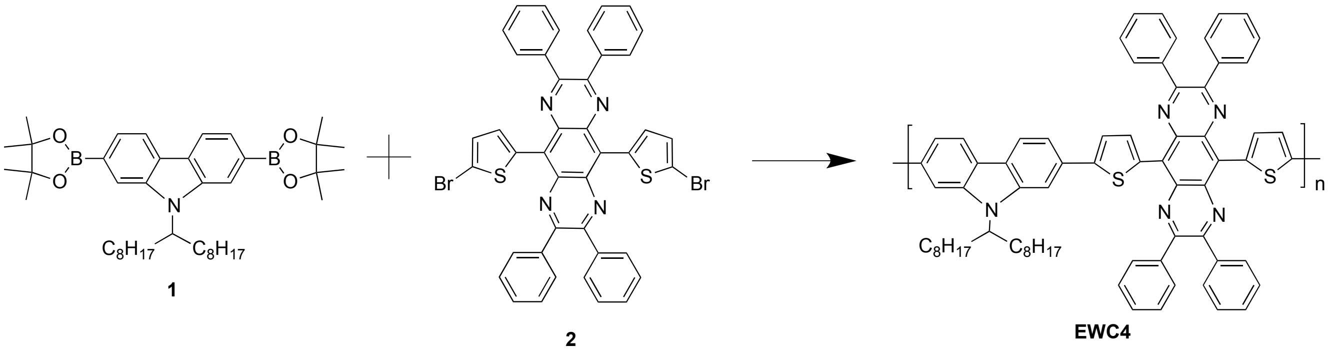

Figure S7. Synthesis steps of EWC4.

The monomer **1**, 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole, and **2**, 5,10-bis(5-bromothiophene-2-yl)-2,3,7,8-tetraphenylpyrazino[2,3-*g*]quinoxaline, were synthesized according to literature.[5,6,7]

In a 25 mL dry flask, monomer **1** (183 mg, 0.28 mmol), monomer **2** (225 mg, 0.28 mmol), Aliquat 336 (50 mg), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) (8 mg), tri(*o*-tolyl)phosphine (P(*o*-Tol)$_3$) (16 mg) and K_3PO_4 (280 mg) were dissolved in a mixture of degassed toluene (5 mL) and deionized water (0.6 mL). The mixture was vigorously stirred at 100 °C for 4 h under nitrogen. The polymer was end-capped by adding 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (204 mg), and after 2 h, bromobenzene (0.3 mL). The mixture was stirred for another 2 h, cooled down and was poured into acetone. The polymer was collected by filtration through 0.45 µm Teflon filter. It was then dissolved in ODCB (100 mL) and mixed with a solution of sodium diethyldithiocarbamate trihydrate (5 g) in deionized water (100 mL). The mixture was stirred at 80 °C overnight under nitrogen. The organic phase was separated and washed three times with water. Then it was poured into acetone (400 mL). The precipitate was collected and was Soxhlet-extracted in order with diethyl ether, dichloromethane and then with chloroform. The chloroform solution was concentrated to a small volume and the polymer was precipitated by pouring this solution into acetone. Finally, the polymer was collected by filtration using a 0.45 µm Teflon filter and dried under vacuum at 40 °C overnight (190 mg, 63%).

Excitations, oscillator strengths and wavelengths

Table S2. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in APFO-3.

Monomer		Dimer		Trimer		Pentamer	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
536.99	0.6468	590.24	1.8103	610.87	2.8247	625.45	4.011
395.42	0.0148	544.26	0.1964	572.88	0.3732	602.06	1.6505
360.97	1.0599	490.05	0.0547	545.09	0.2696	579.78	0.3925
323.4	0.0111	475.75	0.0291				
317.17	0.0051	421.82	0.0147				
316.72	0.0032	403.09	0.0722				
303.96	0.0012	397.25	1.6342				
300.38	0.1013	367.88	0.1388				
295.85	0.0064	363.75	0.085				
286.52	0.0949	358.52	0.0023				
283.67	0.0373	352.37	0.1987				
279.72	0.0065	329.37	0.0078				
269.72	0	324.3	0.0434				
265.4	0.0046	321.73	0.0042				
261.16	0.0223	320.16	0.1221				
		319.32	0.0014				
		317.82	0.0152				
		317.64	0.0127				
		316.03	0.0093				
		308.43	0.0972				

Table S2. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in APFO-15.

Monomer		Dimer		Trimer		Tetramer	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
515.05	0.5328	575.06	1.2721	597.42	1.4439	604.34	1.2819
386.7	0.0335	535.24	0.2808	556.51	1.0573	575.61	1.8294
377.09	0.0271	478.36	0.0567	539.49	0.081	551.28	0.2886
370.23	0.0772	465.63	0.0261			537.61	0.2345
367.01	0.1386	414.71	0.0057			512.4	0.0136
361.54	0.1945	401.34	0.5889			503.88	0.0029
351.61	0.6001	398.23	0.3191			491.23	0.024
325.93	0.104	387.85	0.1534			489.48	0.0149
313.58	0.0092	381.46	0.0609			487.85	0.0581
311.71	0.0379	375.12	0.1636			478.16	0.0023
311.23	0.005	369.03	0.2232			468.28	0.0119
299.74	0.0328	368.57	0.0089			464.91	0.0176
295.6	0.0082	368.14	0.1501			458.95	0.0095
293.13	0.1173	365.67	0.0044			448.65	0.0087
288.92	0.0262	362.09	0.0062			440.5	0.0059
288.32	0.2109	359.01	0.3631			433.96	0.0007
286.93	0.0032	353.21	0.0896			424.74	0.0002
283.27	0.0448	350.21	0.0317			416.88	0.0012
		347.15	0.0013			410.43	0.0991
		339.7	0.0433			409.51	0.9036

		336.8	0.022			403.09	0.9538
		330.77	0.0466			401.45	0.1089
		329.84	0.0179			399.85	0.1538
		329.32	0.0015			392.14	0.0019
		327.06	0.0021			390.59	0.2965
		324.9	0.0177				
		323.66	0.0553				
		322.81	0.0222				
		320.97	0.08				
		318.02	0.0034				
		316.65	0.0072				
		315.26	0.0391				
		313.47	0.0516				
		312.99	0.0171				
		311.9	0.0186				
		310.27	0.0985				
		304.57	0.0014				
		303.1	0.1194				
		301.19	0.0077				
		300.69	0.0095				
		299.62	0.0288				
		298.93	0.1061				
		296.28	0.0087				
		292.31	0.0024				
		291.83	0.0079				

Table S3. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in APFO-G9.

Monomer		Dimer		Trimer		Tetramer	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
702.66	0.3395	773.02	0.8694	804.71	1.3152	808.11	1.6804
487.67	0.0125	716.98	0.1753	754.75	0.3042	774	0.4719
438.32	0.0165	626.15	0.0232	722.65	0.1919	745.33	0.2592
437.74	0.0703			661.36	0.0224	720.8	0.1621
416.58	0.0014			650.57	0.0184	668.71	0.0101
398.26	0.5174			637.66	0.0127	660.22	0.0185
394.48	0.037			611.38	0.0119		
389.6	0.0176			587.44	0.0019		
381.52	0.2546			580.26	0.0012		
375.6	0.8431			532.7	0.0041		
369.37	0.0772			522.14	0.0036		
343.55	0.0047			498.1	0.0154		
339.41	0.0159			465.59	0.0047		
335.96	0.0226			458.96	0.0259		
333.82	0.0125			454.56	0.0018		
333.11	0.1264			446.69	0.0299		
329.22	0.0235			445.28	0.0347		

322.97	0.0058			440.04	0.0858		
322.32	0.0071			438.42	0.0041		
320.38	0.0988			437.71	0.002		
312.22	0.0046			437.42	0.0029		
303.09	0.0513			427.98	0.1352		
301.8	0.0033			424.12	0.3546		
300.76	0.0074						
297.99	0.0075						
293.3	0.1495						
291.15	0.1082						
288.82	0.1491						
288.36	0.0093						
286.97	0.0079						
286.01	0.0006						
282.96	0.0696						
281.32	0.0484						
279.72	0.0168						
276.89	0.0278						

Table S4. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in EWC3.

Monomer		**Dimer**		**Trimer**		**Tetramer**	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
515.55	0.497	565.38	1.203	582.56	1.7836	591.03	2.2547
421	0.003	526.74	0.2658	552.45	0.4309	566.7	0.5201
388	0.0257	470.88	0.0359	527.99	0.3058	548.3	0.508
378.13	0.0126	461.01	0.0306			527.49	0.2751
366.39	0.0371	425.78	0.0027			502.35	0.0066
365.05	0.1186	422.33	0.0041			495.43	0.0115
358.38	0.1733	412.82	0.0082			486.25	0.0139
349.82	0.7374	409.72	0.003			481.11	0.0288
325.28	0.0798	396.97	0.0666			479.7	0.0329
324.22	0.0194	393.29	0.2546			471	0.0088
312.16	0.0306	388.16	0.7849			461.15	0.0152
311.62	0.0011	387.91	0.0533			459.99	0.0101
311.12	0.0024	380.29	0.0513			452.7	0.0123
310.59	0.0218	370.34	0.2258			443.41	0.0051
298.81	0.0334	368.09	0.106			434.96	0.0037
295.28	0.1187	367.48	0.0354			431.1	0.0023
289.3	0.0605	366.7	0.0935			426.01	0.0038
287.51	0.181	362.48	0.0218			425.73	0.0038
284.2	0.0105	361.26	0.0288			423.99	0.0048
281.03	0.047	356.71	0.2591			423.62	0.003
278.78	0.0116	351.23	0.1784			420.38	0.0047
277.72	0.007	348.26	0.0116			414.12	0.0031
273.73	0.0007	344.95	0.0611			413.74	0.0046
269.24	0.0177	339.67	0.0152			411.93	0.0047

267.71	0.0084	337.05	0.0533			411.01	0.0004
		333.06	0.023			408.5	0.0021
		329.2	0.0027			400.17	1.6727
		327.74	0.064			397.42	0.1357
		326.43	0.0036			396.92	0.0458
		325.62	0.0085			394.77	0.0001
		325.07	0.0458				
		323.84	0.0189				
		323.04	0.0647				
		321.93	0.0147				
		316.88	0.0305				
		316.15	0.0541				
		313.37	0.0125				
		313.27	0.013				
		312.48	0.0241				
		311.41	0.0463				
		310.84	0.0078				
		310.33	0.0588				
		309.26	0.0246				

Table S5. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in EWC4.

Monomer		**Dimer**		**Trimer**		**Tetramer**	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
702.86	0.3278	788.51	0.8365	820.58	1.2369	833.07	1.6592
514.9	0.0014	722.37	0.1788	768.12	0.3159	791.32	0.3747
490.73	0.0097	630.04	0.0354	728.9	0.1986	761.41	0.2949
438.28	0.007	614.93	0.0062	671.72	0.0233	725.44	0.1944
437.62	0.0659	531.02	0.0032	659.43	0.0198		
414.22	0.0016	519.58	0.0006	645	0.0206		
398.78	0.5302	514.7	0.0017	614.09	0.0138		
394.69	0.0247	504.46	0.0008	592.4	0.0033		
390.73	0.0269	499.49	0.0104	582.3	0.0019		
381.08	0.2776	464.96	0.0001	539.08	0.0043		
370.25	0.7303	448.73	0.0098	527.95	0.0039		
366.43	0.1395	446.71	0.0178	518.82	0.001		
342.47	0.0096	440.45	0.0281	516.97	0.0022		
336.34	0.0062	439.91	0.0607	516.5	0.0004		
333.86	0.1412	437.07	0.0022	508.08	0		
332.38	0.0382			505.97	0.0007		
329.08	0.0147			500.81	0.0105		
327.8	0.0229			472.29	0.0031		
326.47	0.0128			469.93	0.0024		
323.18	0.1027			463.56	0.0082		
320.81	0.0144			462.46	0.0153		
316.15	0.0006			459.27	0.0007		
311.14	0.0036			458.57	0.0005		

304	0.0103			455.88	0.0002		
301.78	0.0077			450.29	0.007		
301.6	0.0337			449.64	0.0124		
300.41	0.0056			439.65	0.0588		
298.1	0.0024			438.4	0.0044		
292.88	0.0918			437.64	0.0036		
290.42	0.0914			436.94	0.0042		
289.58	0.0233						
288.91	0.1633						
285.75	0.0009						
282.56	0.0959						
280.07	0.0146						
279.37	0.0118						
278.43	0.002						
277.06	0.0313						
275.47	0.1539						
273.45	0.0047						

Table S6. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in BDT-Q.

Monomer		**Dimer**		**Trimer**		**Pentamer**	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
484.94	0.207	572	0.7313	614.6	1.5663	644.95	3.2308
395.16	0.1659	517.02	0.1449	556.84	0.1044	601.9	0.0051
369.29	0.4004	497.89	0.1012	535.88	0.0304	569.16	0.2862
363.56	0.0286	449.94	0.4772	523.39	0.1815	552.36	0.0081
361.02	0.0229	429.04	0.0038	504.01	0.1019	548.77	0.1511
356.79	0.0148	403.19	0.0795	480.08	0.0511	539.73	0.0192
349.48	0.0772	391.46	0.0079	467.8	0.5055	535.62	0.0374
332.17	0.0035	389.32	0.2676	460.5	0.1758		
329.02	0.0145	385.73	0.1134	450.41	0.0052		
321.94	0.0031	377.9	0.1681	439.71	0.0155		
318.57	0.0527	373.33	0.3113	410.06	0.0249		
308.94	0.2513	371.86	0.0944	407.97	0.1165		
300.91	0.0028	369.25	0.0025	405.21	0.0334		
295.52	0.2625	367.01	0.0159	399.46	0.389		
291.17	0.0414	364.7	0.02	395.22	0.0156		
290.23	0.0258	363.14	0.0202	392.32	0.0322		
289.68	0.0857	361.68	0.0398	389.98	0.1426		
287.35	0.0979	356.24	0.0056	386.3	0.141		
282.25	0.0012	355.28	0.0241	383.62	0.0324		
281.71	0.0175	354.41	0.0563				
		351.98	0.0062				
		350.51	0.0259				
		347.81	0.0018				
		343.95	0.1567				
		342.55	0.0807				

		340.26	0.0109				
		332.62	0.0291				
		332.13	0.0233				
		331.07	0.0198				
		329.45	0.0064				
		325.88	0.1009				
		324.03	0.0186				
		323.84	0.1295				
		322.32	0.1424				
		320.85	0.1101				
		319.27	0.0735				
		318.69	0.0677				
		315.83	0.0081				
		314.33	0.0014				
		310.05	0.0031				
		308.82	0.0257				
		305.52	0.0075				

Table S7. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in BDT-T-TP-T.

Monomer		**Dimer**		**Trimer**		**Pentamer**	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
643.42	0.5309	754.04	1.8303	801.91	3.2254	836.21	5.9256
504.65	0.0208	660.08	0.1065	718.85	0.0012	782.52	0.0059
435.74	0.4402	609.01	0.0099	666.32	0.1806	734.2	0.4412
422.38	0.0625	562.8	0.0498				
410.4	0.0884	534.1	0.0037				
394.06	0.0252	513.91	0.0873				
382.85	0.0139	493.56	0.0036				
370.97	0.2204	473.72	0.8407				
367.78	0.0054	453.95	0.1874				
359.36	0.3089	452.32	0.1296				
355.57	0.1674	443.82	0.0853				
350.91	0.4115	427.3	0.0081				
341.7	0.0235	424.07	0.0311				
324.43	0.0104	421.67	0.022				
321.92	0.0173	412.39	0.0773				
318.15	0.0064	407.43	0.0175				
316.77	0.0119	396.57	0.0192				
313.57	0.0662	392.27	0.0497				
308.68	0.0274	388.18	0.0029				
306.28	0.0242	387.03	0.0068				
		385.62	0.0172				
		384.43	0.0628				
		382.83	0.0046				
		380.33	0.0373				
		375.69	0.0663				

		373.99	0.1756				
		372.08	0.0419				
		370.79	0.456				
		367.57	0.0045				
		366.29	0.1604				
		365.38	0.0534				
		362.05	0.1994				
		361.15	0.018				
		360.85	0.0478				
		356.19	0.0282				
		355.97	0.1787				
		354.16	0.2657				
		350.56	0.0093				
		348.15	0.0028				
		346.39	0.0451				
		344.71	0.0145				
		343.29	0.0298				
		338.49	0.011				
		337.23	0.0355				
		335.38	0.0048				
		332.61	0.0044				

Table S8. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in BDT-BTz.

Monomer		Dimer		Trimer		Pentamer	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
400.74	0.2852	494.44	1.637	542.01	3.0103	581.79	5.5611
339.87	0.4438	444.92	0.0386	472.11	0.0025	525.79	0.0042
299.41	0.1665	403.43	0.5391	454.82	0.0086	493.29	0.0036
275.25	0.0321			452.59	0.0735	485.19	0.38
271.55	0.0025			418.57	0.3183	468.52	0.2263
263	0.0816			410.56	0.443	465.79	0.0209
260.61	0.0305			399.21	0.0427		
248.77	0.2029			397.3	0.0038		
243.47	0.0133			391.58	0.0213		
239.55	0.0019			367.25	0.0025		
238.22	0.0109			361.09	0.0004		
233.97	0.0023			358.45	0.1246		
232.59	0.0037			346.81	0.1488		
226.62	0.0206			336.57	0.0096		
225.74	0.031			329.03	0.0169		
224.5	0.0097			326.55	0.0175		
221.98	0.1155			319.77	0.0027		
218.76	0.1072			312.91	0.057		
217.32	0.0691			312.11	0.1092		
216.9	0.0321			306.98	0.0652		
				305.77	0.2216		

				299.28	0.0211		
				296.43	0.0138		
				293.66	0.1395		
				291.73	0.001		
				291.33	0.0075		

Table S9. Calculated wavelengths λ and oscillator strengths f for the relevant excitations in TQ1.

Monomer		**Dimer**		**Trimer**		**Tetramer**		**Pentamer**	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
390.61	0.1315	496.61	0.4625	549.82	1.0025	579.12	1.5258	595.97	2.0828
357.47	0.0253	428.02	0.0441	479.1	0.0045	505.65	0.013	533.97	0.0172
351.79	0.0314	402.23	0.0232	441.42	0.0466	473.88	0.0386	495.56	0.0362
344.39	0.0671	393.22	0.0829	433.25	0.0112	469.37	0.005	486.96	0.006
324.05	0.0093	386.9	0.0336	409.48	0.0375	445.38	0.0489	471.74	0.0099
304.31	0.1879	366.09	0.0482	403.6	0.0201	431.03	0.0446	459.21	0.1329
294.22	0.0787	364.82	0.0103	394.12	0.004	413.81	0.0154	445.23	0.0315
290.05	0.0877	362.33	0.0075	390.79	0.0195	405.59	0.0345	431.8	0.0028
280.05	0.0571	358.79	0.0038	388.59	0.0251	402.92	0.0404	428.48	0.0127
278.32	0.0521	353.95	0.0362	382.49	0.0443	400.54	0.0016	416.94	0.0107
275.05	0.0031	349.35	0.0303	371.2	0.0031	397.41	0.0129	410.61	0.0202
265.59	0.3613	339.12	0.0068	369.28	0.057	392.16	0.0239	406.76	0.0033
262.14	0.0529	337.55	0.0215	366.52	0.0096	386.95	0.0068	405.72	0.0444
251.08	0.06	331.61	0.0042	365.75	0.0206	385.96	0.0177	403.41	0.0267
248.4	0.0337	328.54	0.1656	363.8	0.0069	378.21	0.0432	402.08	0.007
245.59	0.0227	325.78	0.0225	361.69	0.0206	376.52	0.0015	396.4	0.058
242.46	0.0006	324.09	0.0774	359.26	0.0895	374.2	0.0038	393.82	0.0078
240.66	0.0102	319.35	0.3206	358.77	0.0056	372.43	0.0032	392.62	0.0301
239.49	0.0246	317.28	0.0812	355.81	0.0042	372.19	0.0217	390.25	0.0122
235.81	0.0296	314.28	0.023	352.66	0.0054	369.12	0.0262	388.54	0.0272
		308.03	0.0772	351.22	0.0028	367.06	0.0187	384.57	0.0067
		304.1	0.0175	349.29	0.04	365.45	0.0244	380.82	0.002
		303.88	0.153	345.56	0.2472	364.67	0.035	378.21	0.0022
		299.62	0.0435	343.59	0.0721	363.57	0.0732	376.06	0.0026
		297.5	0.0092	341.76	0.1096	361.15	0.0217	374.2	0.0094
				340.41	0.0238	360.19	0.0362	373.9	0.0117
				338.63	0.0591	358.92	0.0243	372.55	0.0067
				336.01	0.1545	356.74	0.0129	371.52	0.0127
				334.53	0.016	355.11	0.0071	368.96	0.0324
				333.14	0.0727	354.35	0.0282	367.66	0.0428
				331.21	0.1966	353.15	0.029	367.38	0.0173
				329.77	0.0516	350.81	0.3789	366.75	0.006
				321.28	0.024	349.63	0.1347	365.06	0.0386
				319.84	0.019	348.56	0.0044	364.8	0.0677
				318.15	0.0378	346.65	0.0271	364.05	0.0025
				314.5	0.0221	345.33	0.0156	363.34	0.0092
				312.73	0.0098	343.51	0.1994	362.11	0.0944

				312.37	0.0084	342.14	0.0704	359.84	0.0025
				312.15	0.0242	341.2	0.0765	358.8	0.0004
				309.95	0.0322	338.6	0.0436	358.3	0.0591
				308.23	0.0043	337.43	0.009	357.11	0.0052
				307.34	0.0229			356.43	0.0088
				306.93	0.0076				
				306.01	0.0749				
				303.98	0.008				
				303.72	0.0159				
				303.25	0.0684				
				302.03	0.0738				
				300.53	0.0441				
				299.12	0.0151				

Hexamer		**Heptamer**		**Octamer**		**Nonamer**	
λ [nm]	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**	**λ [nm]**	**f**
606.27	2.5849	614.7	3.1755	622.68	3.7345	626.84	4.2989
550.83	0.0335	565.99	0.0147			591.46	0.0154

Polarizable continuum model (PCM) solvent absorption calculations

Table S3. Solvatochromic shifts of 4 of the polymers at different oligomer sizes. Calculated as the difference in first transition energy from TD-DFT with and without o-DCB PCM.

E_{abs}(PCM)-E_{abs}(vacuum) [meV]							
n	1	2	3	4	5	6	9
BDT-BTz	-3.3	-44.2	-31.0		-7.2		
TQ1		-41.8	-44.9	-36.6		-22.5	-12.7
APFO-G9	2.7	20.7	31.6	36.2			
TBDT-Q	15.4	16.1	13.5		23.1		

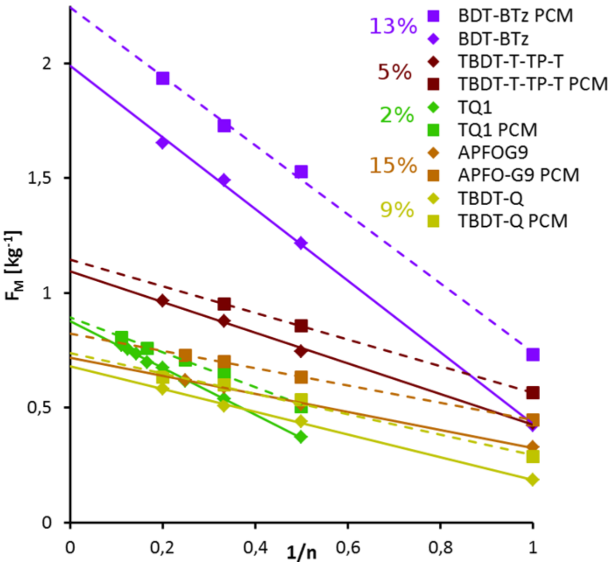

Figure S8. Calculated F_M with and without PCM solvent for 5 of the polymers. The F_M increase upon adding solvent is indicated in %.

Supporting Information References

(1) Barford, W. *Electronic and Optical Properties of Conjugated Polymers*; Oxford University Press: Oxford, 2013.
(2) Tanimoto, A.; Yamamoto, T. *Adv. Synth. Catal.* **2004**, *346*, 1818–1823.
(3) Hou, J.; Chen, H.-Y.; Zhang, S.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J. Am. Chem. Soc.* **2009**, *131*, 15586–15587.
(4) Hellstrom, S.; Lindgren, L. J.; Zhou, Y.; Zhang, F.; Inganas, O.; Andersson, M. R. *Polym. Chem.* **2010**, *1*, 1272–1280.
(5) Blouin, N.; Michaud, A.; Gendron, D.; Wakim, S.; Blair, E.; Neagu-Plesu, R.; Belletête, M.; Durocher, G.; Tao, Y.; Leclerc, M. *J. Am. Chem. Soc.* **2008**, *130*, 732–742.
(6) Zhang, F.; Bijleveld, J.; Perzon, E.; Tvingstedt, K.; Barrau, S.; Inganas, O.; Andersson, M. R. *J. Mater. Chem.* **2008**, *18*, 5468–5474.
(7) Wang, E.; Hou, L.; Wang, Z.; Hellström, S.; Mammo, W.; Zhang, F.; Inganäs, O.; Andersson, M. R. *Org. Lett.* **2010**, *12*, 4470–4473.