Supporting Information

Highly Fluorescent Purine-Containing Conjugated Copolymers with Tailored Optoelectronic Properties

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NMR Spectra of Small Molecules and Monomers

2,6-dichloro-9-hexyl-9H-purine:



Figure S1. ¹H NMR spectrum of 2,6-dichloro-9-hexyl-9*H*-purine (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.87 (t, 3H, CH₃), 1.31 (m, 6H, CH₂), 1.91 (p, 2H, CH₂), 4.25 (t, 2H, NCH₂), 8.09 (s, 1H, C8H).





Figure S2. ¹H NMR spectrum of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine (**M1**) (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.88 (t, 6H, CH₃), 1.19-1.52 (m, 18H, CH₂), 1.75 (p, 4H, CH₂), 1.96 (p, 2H, CH₂), 3.31 (t, 2H, ArCH₂), 3.44 (t, 2H, ArCH₂), 4.28 (t, 2H, NCH₂), 7.00 (d, 1H, ArH), 7.09 (d, 1H, ArH), 7.31 (d, 1H, ArH), 7.54 (d, 1H, ArH), 8.02 (s, 1H, C8-H).



Figure S3. ¹³C NMR spectrum (500 MHz, 25 °C, CDCl₃) of 9-hexyl-2,6-bis(3-hexylthiophen-2-yl)-9*H*-purine (**M1**).



Figure S4. ¹H NMR spectrum of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9*H*-purine (**M2**) (500 MHz, 25 °C, CDCl₃). δ, ppm: 0.89 (m, 6H, CH₃), 1.17-1.54 (m, 18H, CH₂), 1.70 (p, 4H, CH₂), 1.95 (p, 2H, CH₂), 3.24 (t, 2H, ArCH₂), 3.34 (t, 2H, ArCH₂), 4.24 (t, 2H, NCH₂), 6.95 (s, 1H, ArH), 7.05 (s, 1H, ArH), 8.01 (s, 1H, C8-H).



Figure S5. ¹³C NMR spectrum (500 MHz, 25 °C, CDCl₃) of 2,6-bis(5-bromo-3-hexylthiophen-2-yl)-9-hexyl-9*H*-purine (**M2**).

Direct Analysis in Real Time - Mass Spectrometry of M1 and M2



Figure S6. AccuTOF DART-MS analysis of M1. calc'd [M+H⁺]: 537.3080, found: 537.2793.



Figure S7. AccuTOF DART-MS analysis for **M2**. calc'd [M+H⁺]: 693.1290, found: 693.0957.

Sample	Yield (%)	M_n (kg/mol)	M_w (kg/mol)	Ð	λ_{\max}^{abs}	λ_{onset}^{abs}
	68%	4.5	7.9	1.8	424	491
Р1трт	71%	9.0	19.5	2.2	424	492
	83%	10.1	16.7	1.7	423	492
D2_	57%	4.6	6.0	1.3	412	459
P2F	80%	9.4	17.5	1.9	416	479
	42%	5.0	16.7	3.3	423	477
P3 _{TFT}	55%	5.3	7.4	1.4	425	482
	48%	12.1	38.5	3.2	441	500
	50%	5.0	7.6	1.5	423	494
$\mathbf{P4_{T}}$	53%	9.8	16.9	1.7	426	514
	61%	18.0	37.8	2.1	425	514
	69%	4.4	6.8	1.5	455	531
P5prodot	42%	9.8	20.5	2.1	458	532
	86%	18.3	38.5	2.1	458	533
Рбтвтт	47%	12.5	31.8	2.5	400	569

Table S1. Molecular Weights, Yields, and Absorption Characteristics of Purine-containing Copolymers Synthesized via DArP.*

*Data in bold identifies the copolymer that was used for optoelectronic characterizations.

¹H NMR Spectra of Purine-Containing Copolymers



Figure S8. ¹H NMR spectrum of **P1**_{TPT} (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.50-2.15, 3.21-3.63, 4.02-4.45, 6.89-7.70, 7.87-8.20. The copolymer was obtained as an orange solid. A trace amount of DMAC is observed at ~3.0 ppm.



Figure S9. ¹H NMR spectrum of **P2**_F (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.51-2.19, 3.17-3.72, 4.95-5.25, 6.86-7.88, 8.00-8.18. The copolymer was obtained as a dark green solid. A trace amount of DMAC is observed at ~3.0 ppm.



Figure S10. ¹H NMR spectrum of **P3**_{TFT} (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.61-2.19, 3.23-3.79, 4.16-5.37, 7.01-7,73, 8.03-8.13. The copolymer was obtained as a green solid.



Figure S11. ¹H NMR spectrum of **P4**_T (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.46-2.98, 3.21-3.95, 4.11-4.38, 6.43-7.74, 7.81-8.13. The copolymer was obtained as a dark orange solid.



Figure S12. ¹H NMR spectrum of **P5**_{ProDOT} (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.53-2.15, 2.21-2.53, 3.11-3.67, 4.02-4.58, 6.91-7.44, 7.87-8.08. The copolymer was obtained as a red solid.



Figure S13. ¹H NMR spectrum of **P6**_{TBTT} (300 MHz, 25 °C, CDCl₃). δ (ppm): 0.31-2.95, 3.12-3.99, 4.20-4.51, 6.52-8.27. The copolymer was obtained as a dark purple solid.

GPC Traces of Purine-containing Copolymers

The following elugrams are from the copolymers presented in Table 1 of the *Article*. All samples were measured using THF at 25 °C as the mobile phase at a flow rate of 1 mL/min, and molecular weight values are reported relative to PS standards. The concentration of samples was nominally 5 mg/mL.



Figure S14. GPC trace of P1_{TPT}. P1_{TPT} has an $M_n = 9.03$ kg/mol and D = 2.16.



Figure S16. GPC trace of P3_{TFT}. P3_{TFT} has an $M_n = 12.1$ kg/mol and D = 3.18.



Figure S15. GPC trace of P2_F. P2_F has an $M_n = 9.46$ kg/mol and D = 1.81.



Figure S17. GPC trace of $P4_T$. P4_T has an $M_n = 9.82$ kg/mol and D = 1.72.



Figure S18. GPC trace of P5_{ProDOT}. P5_{ProDOT} has an $M_n = 9.79$ kg/mol and D = 2.06.



Figure S19. GPC trace of P6_{TBTT}. P6_{TBTT} has an $M_n = 12.5$ kg/mol and D = 2.54.

Absorption Spectra as a Function of Copolymer Molecular Weight

The following UV/Vis spectra provide insight into changes in absorption behaviors of the various purine-containing copolymers as a function of copolymer molecular weight. All spectra were acquired at a nominal concentration of 0.01 mg/mL in CHCl₃. Absorption maxima and onsets are summarized in Table S1.



Figure S20. Normalized UV-Vis spectra of **P1**_{TPT} copolymers synthesized at $M_n = 4.5$ g/mol, 9.0 g/mol, and 10.1 g/mol, as indicated in the legend.



Figure S21. Normalized UV-Vis spectra of P2_F copolymers synthesized at $M_n = 4.6$ g/mol and 9.4 g/mol, as indicated in the legend.



Figure S22. Normalized UV-Vis spectra of **P3**_{TFT} copolymers synthesized at $M_n = 5.0$ g/mol, 5.3 g/mol, and 12.1 g/mol, as indicated in the legend.



Figure S23. Normalized UV-Vis spectra of P4_T copolymers synthesized at $M_n = 5.0$ g/mol, 9.8 g/mol, and 18.0 g/mol, as indicated in the legend.



Figure S24. Normalized UV-Vis spectra of **P5**_{ProDOT} copolymers synthesized at $M_n = 4.4$ g/mol, 9.8 g/mol, 18.3 g/mol, as indicated in the legend.

Absorbance and Corresponding Beer-Lambert Plots

The following plots present concentration dependent optical absorption data and Beer-Lambert plots for **M1** and for the purine-containing polymers presented in Table 1 of the *Article*.



Figure S25. UV-Vis spectra of TPT (M1) at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.



Figure S26. UV-Vis spectra of **P1**_{TPT} at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.



Figure S27. UV-Vis spectra of $P2_F$ at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.



Figure S28. UV-Vis spectra of $P3_{TFT}$ at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.



Figure S29. UV-Vis spectra of $P4_T$ at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.



Figure S30. UV-Vis spectra of $P5_{ProDOT}$ at various concentrations in chloroform (left) and the corresponding the Beer-Lambert plot (right) with best-fit line.



Figure S31. UV-Vis spectra of **P6**_{TBTT} at various concentrations in chloroform (left) and the corresponding Beer-Lambert plot (right) with best-fit line.

Methanol Titration Study of P5ProDOT in Chloroform



Figure S32. UV-Vis spectra of $P5_{ProDOT}$ in CHCl₃ acquired after sequential additions of methanol are used to investigate whether shoulder at 500 nm is due to aggregation. The fact that the absorbance maximum and shape remain unchanged suggests that the shoulder is not due to increased aggregation.

Solvatochromic Behavior of Purine-containing Copolymers



Figure S33. UV-Vis spectra of P1_{TPT} in THF, DMF, and CHCl₃.



Figure S34. UV-Vis spectra of P2_F in THF, DMF, and CHCl_{3.}



Figure S35. UV-Vis spectra of P3TFT in THF, DMF, and CHCl₃.



Figure S36. UV-Vis spectra of P4T in THF, DMF, and CHCl₃.



Figure S37. UV-Vis spectra of P5ProDOT in THF, DMF, and CHCl₃.



Figure S38. UV-Vis spectra of P6TBTT in THF, DMF, and CHCl₃.

Cyclic Voltammograms of Purine-containing Copolymers and M1



Figure S39. Cyclic voltammogram of TPT (**M1**) in solution. Measured in dichloromethane using a scan rate of 150 mV/s with $(nBu)_4NPF_6$ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.



Figure S40. Cyclic voltammogram of **P1**_{TPT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with $(nBu)_4NPF_6$ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.



Figure S41. Cyclic voltammogram of **P3**_{TFT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with $(nBu)_4NPF_6$ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.



Figure S42. Cyclic voltammogram of **P4**_T as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with $(nBu)_4NPF_6$ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.



Figure S43. Cyclic voltammogram of **P5**_{ProDOT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with $(nBu)_4NPF_6$ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.



Figure S44. Cyclic voltammogram of **P6**_{TBTT} as a thin film. Measured in acetonitrile using a scan rate of 150 mV/s with $(nBu)_4NPF_6$ (at 0.20 M) as the supporting electrolyte. Potential is set relative to Fc/Fc⁺.

Computiational Results

		HOMO	LUMO
System	Method	(eV)	(eV)
	B3LYP/cc-pvdz	-5.73	-1.81
M1	m06-2X/cc-pvdz	-7.03	-0.95
	DFTB	-5.32	-2.68
Р1трт	B3LYP/6-31G*	-4.93	-2.06
	DFTB	-4.77	-2.93

Table S2. Molecular Orbital Energy Levels Calculated by Various DFT-Based Levels of Theory.



Figure S45. Pictures of optimized structures perpendicular to the main chain of **P1**_{TPT} calculated by a) DFTB and by b) DFT using B3LYP/6-31G*. The structures are approximately planar, with the largest dihedral angle along the backbone being 15°, and the similarity suggests good accuracy of DFTB. The optimized structure of **M1** calculated by B3LYP/cc-pvdz is shown in c), and it shows that the flanking thienyl at C2 is coplanar with the purine, while the flanking thienyl at C6 is rotated out of plane by 30°.