Electronic Supporting Information

Monomer Stoichiometry Imbalance-Promoted Formation of Multisubstituted Polynaphthalenes by Palladium-Catalyzed Polycouplings of Aryl Iodides and Internal Diynes

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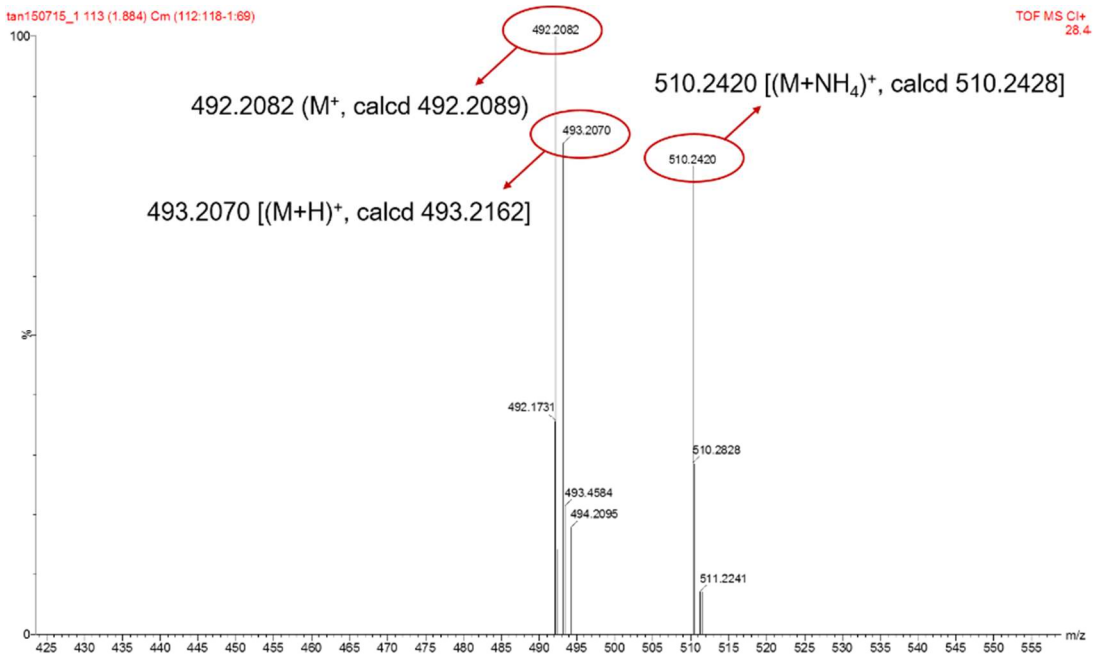

Figure S1. High-resolution mass spectrum of **4**.

Table S1. Effect of catalyst loading on the polymerization of 1a and 2a[a]

No.	[$Pd(OAc)_2$] (M)	[**1a**]:[**2a**]	Yield (%)	M_n[b]	M_w[b]	PDI[b]
1[c]	0.02	1.25:1	98.5	13 200	43 400	3.3
2	0.04	1.25:1	94.8	15 900	43 800	2.8
3	0.06	1.25:1	Gel			
4	0.04	1:1	Gel			
5	0.04	1.5:1	86.9	12 500	39 100	3.1

[a] Carried out in *o*-xylene under nitrogen at 80 °C in the presence of $Pd(OAc)_2$, Ag_2CO_3 and P(2-furyl)$_3$. [**2a**] = 0.20 M, [Ag_2CO_3] = 0.40 M. [P(2-furyl)$_3$] = 0.06 M. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. PDI = polydispersity index = M_w/M_n. [c] Data taken from Table 1, no. 3.

Table S2. Time course on the polymerization of 1a and 2a[a]

No.	Time (h)	Yield (%)	M_n[b]	M_w[b]	PDI[b]
1	1	3.8	2 300	2 800	1.2
2	3	94.1	11 300	27 200	2.4
3	6	95.0	11 600	30 300	2.6
4	12	98.0	12 200	36 500	3.0
5	18	99.0	12 900	40 100	3.1
6[c]	24	98.5	13 200	43 400	3.3
7	30	99.1	13 400	48 100	3.6

[a] Carried out in *o*-xylene under nitrogen at 80 °C in the presence of $Pd(OAc)_2$, Ag_2CO_3 and P(2-furyl)$_3$. [**1a**] = 0.25 M, [**2a**] = 0.20 M, [Pd] = 0.01 M, [Ag_2CO_3] = 0.20 M. [P(2-furyl)$_3$] = 0.03 M. [b] Determined by GPC in THF on the basis of a linear polystyrene calibration. PDI = polydispersity index = M_w/M_n. [c] Data taken from Table 1, no. 3.

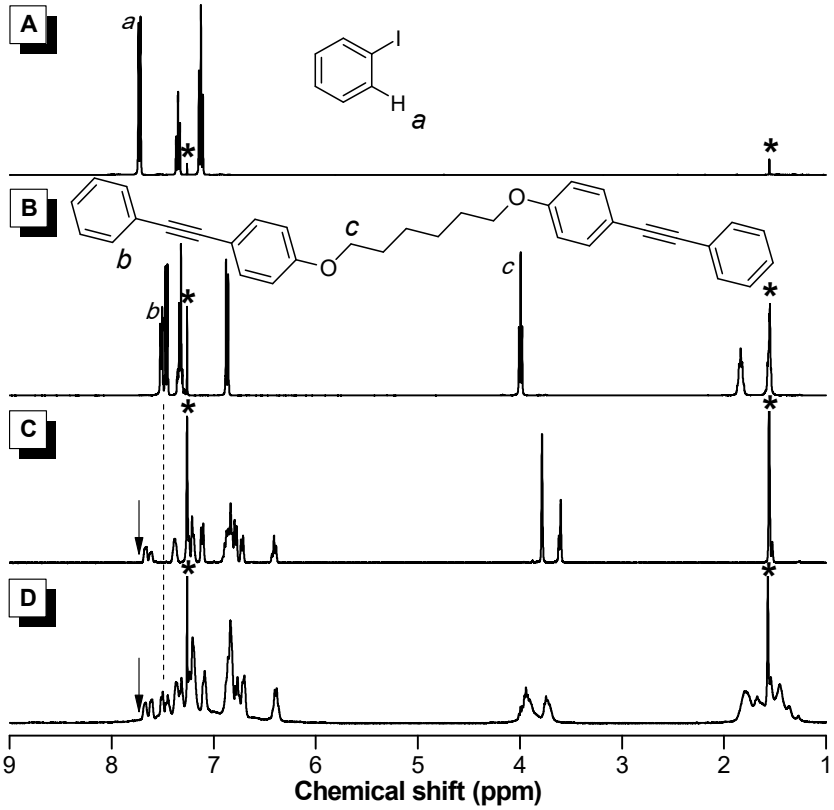

Figure S2. ^{1}H NMR spectra of (A) **1a**, (B) **2a**, (C) **4** and (D) P**1a**/**2a** (sample taken from Table 1, no. 2) in chloroform-*d*.

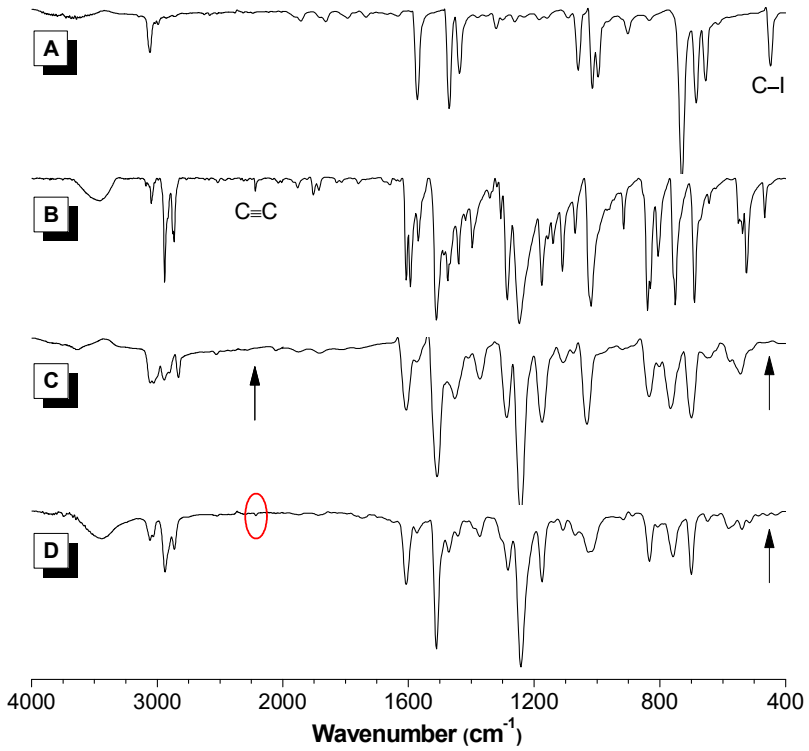

Figure S3. IR spectra of (A) **1a**, (B) **2a**, (C) **4** and (D) P**1a**/**2a** (sample taken from Table 1, no. 2).

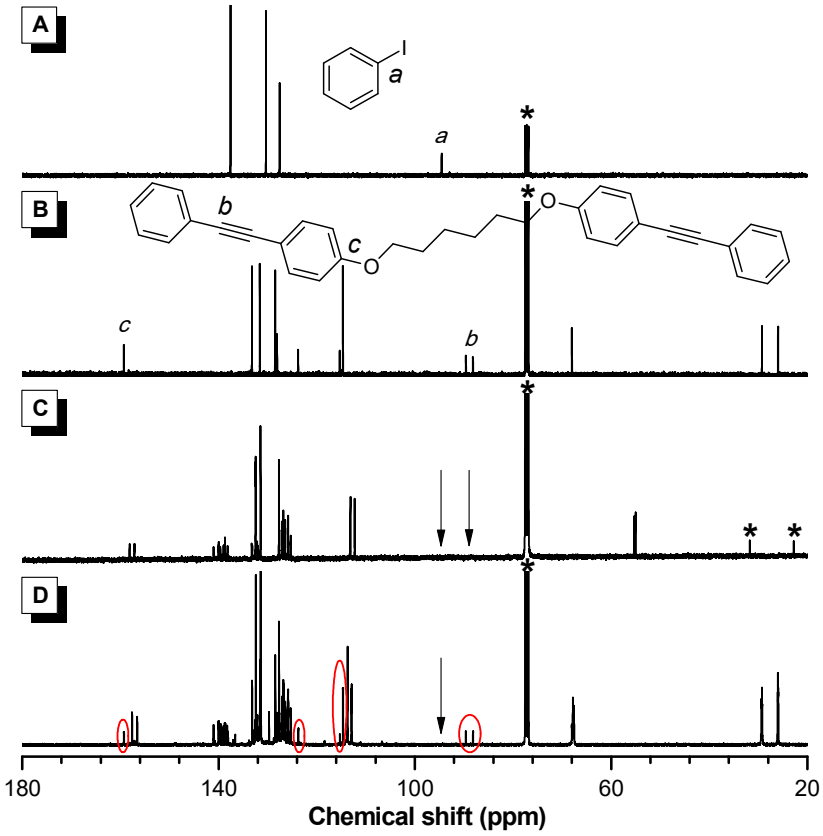

Figure S4. ^{13}C NMR spectra of (A) **1a**, (B) **2a**, (C) **4** and (D) P**1a**/**2a** (sample taken from Table 1, no. 2) in chloroform-*d*.

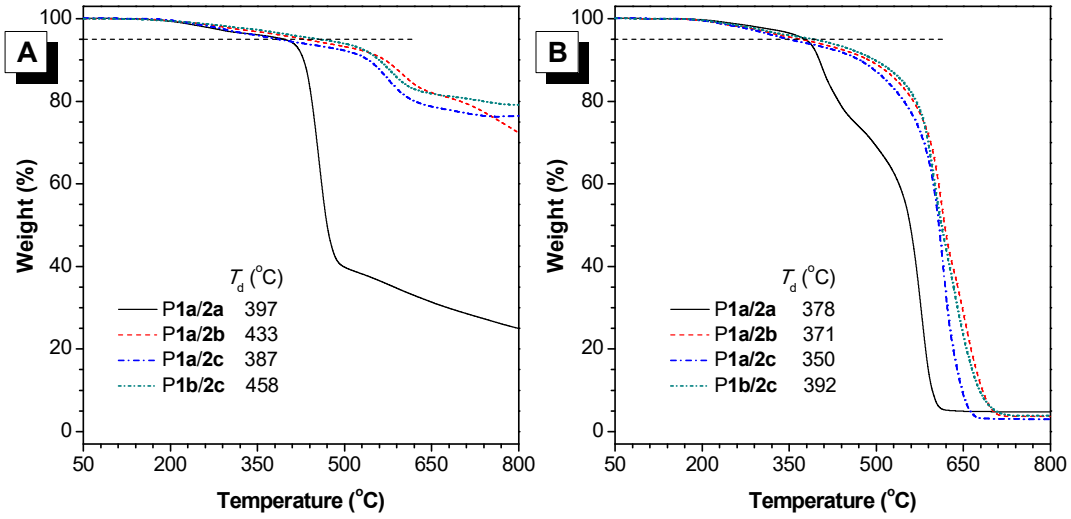

Figure S5. TGA thermograms of P**1**/**2** (samples taken from Table 4) recorded (A) under nitrogen and (B) under air at a heating rate of 10 °C/min.

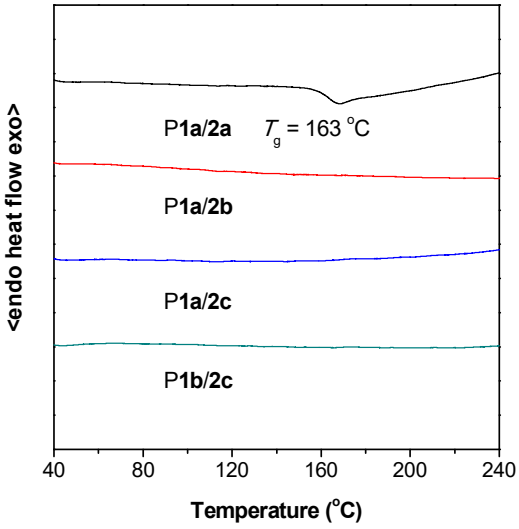

Figure S6. DSC thermograms of P**1**/**2** recorded under nitrogen during the second heating cycle at a heating rate of 10 °C/min.

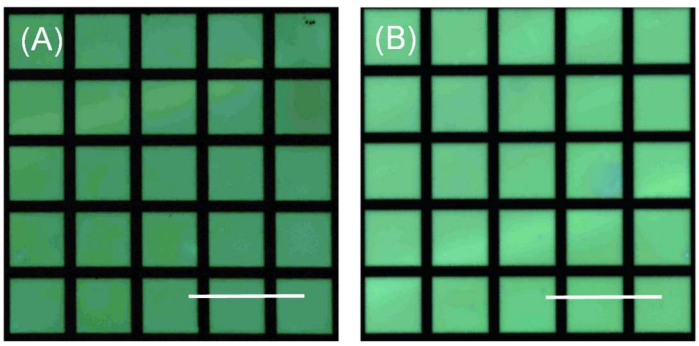

Figure S7. Two-dimensional fluorescent photopatterns of (A) **2b** and (B) **2c** taken under UV light illumination. Scale bar: 200 μm; excitation wavelength: 330–385 nm.