

Supporting Information

Engineering Topochemical Polymerizations Using Block Copolymer Templates

*Liangliang Zhu,¹ Helen Tran,¹ Frederick L. Beyer,² Scott D. Walck,² Xin Li,³ Hans Ågren,³ Kato L. Killops,^{*4} Luis M. Campos^{*1}*

1) Department of Chemistry, Columbia University, New York, New York, 10027, United States

2) Army Research Laboratory, Aberdeen Proving Ground, Maryland 21005, United States

3) Division of Theoretical Chemistry and Biology, School of Biotechnology, KTH Royal Institute of Technology, SE-10691 Stockholm, Sweden

4) Edgewood Chemical Biological Center, Aberdeen Proving Ground, Maryland 21010, United States

Synthetic route of the IDA mesogen:

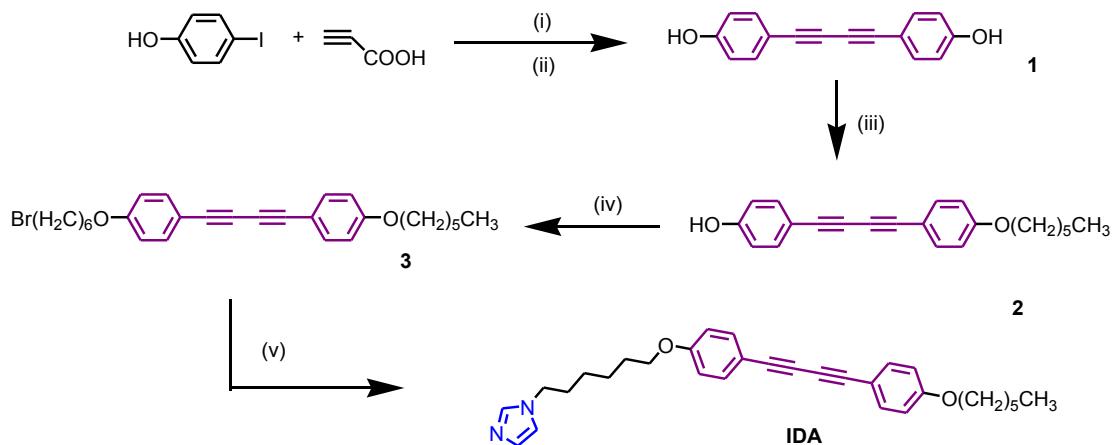


Figure S1. Synthetic route for the preparation of the monomer IDA. (i) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , Et_3N , DMF, (ii) Ag_2CO_3 , heating, (iii) hexyl bromide, K_2CO_3 , (iv) dibromoalkane, K_2CO_3 and (v) imidazole, KOH .

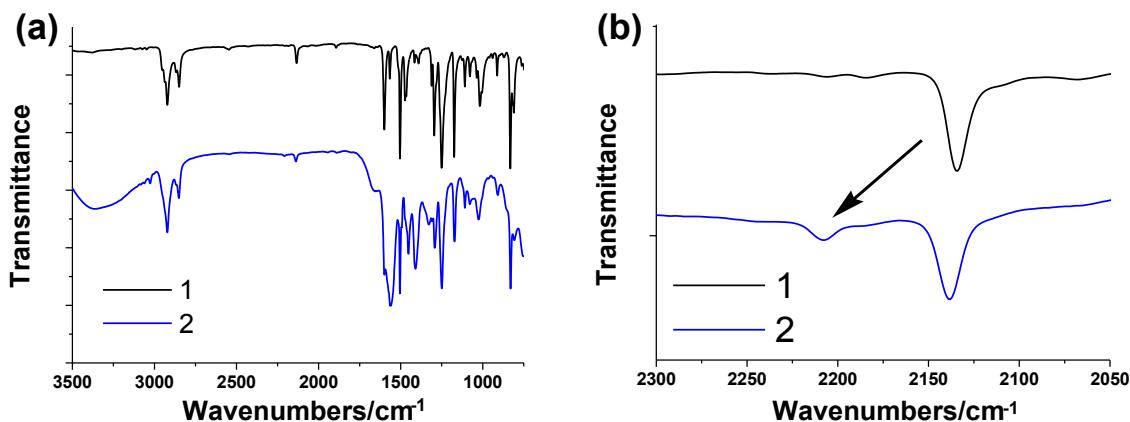
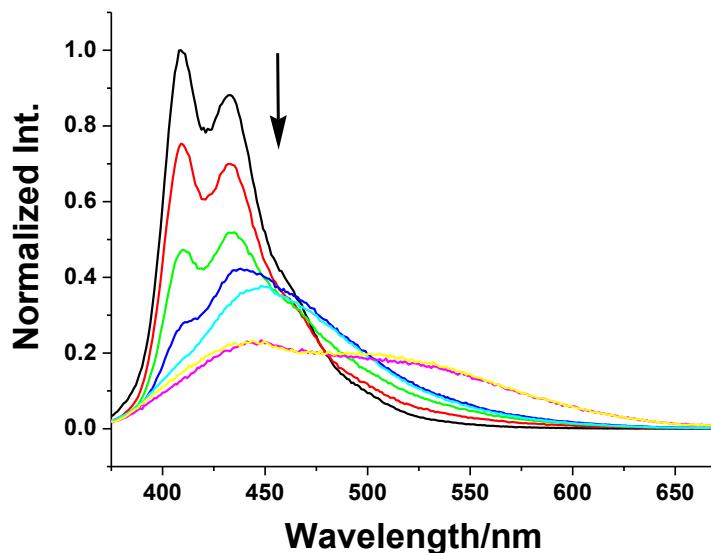


Figure S2. (a) IR spectra of (1) IDA and (2) PS-*b*-(PAA-*sg*-IDA) after irradiation at 254 nm. (b) IR spectra of the diacetylene vibration range.

A)



B)

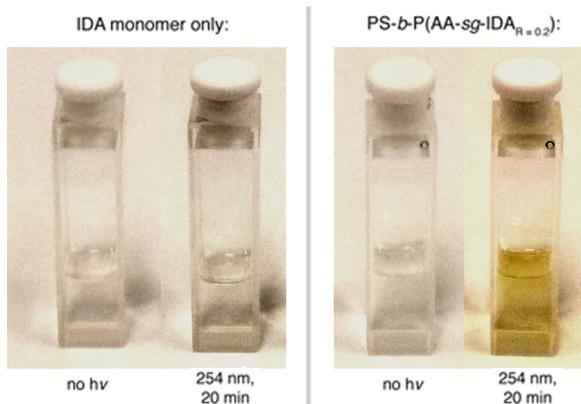


Figure S3. A) Photoluminescence emission spectra recorded at various time intervals, up to 20 min when the reaction mixture reached a photostationary state ($\lambda_{\text{ex}} = 365$ nm) of PS-*b*-(PAA-sg-IDA_{R=0.2}) solution at 40 μM . B) Photograph under an ambient light of solutions of IDA monomer and PS-*b*-P(AA-sg-IDA_{R=0.2}) in chloroform before and after irradiation at 254 nm for 20 min, respectively. The concentration is 7 mM as calculated by IDA.

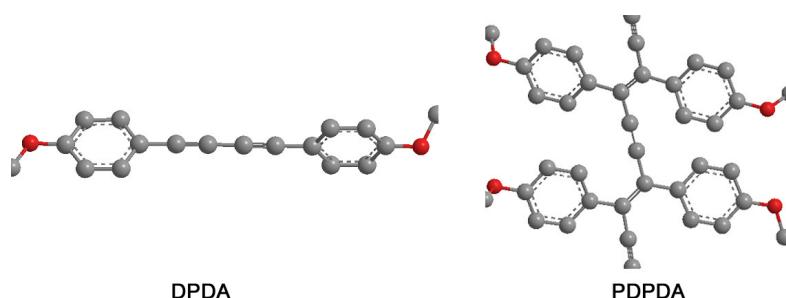


Figure S4. Molecular models of the DPDA and PDPDA.

Table S1. Energy levels of frontier molecular orbitals and HOMO-LUMO energy gaps, computed at the B3LYP/6-31G* level of theory.

Compound	E(HOMO) / eV	E(LUMO) / eV	ΔE / eV
monomer model	-5.12	-1.26	3.86
Polydiacetylene model	-4.76	-1.96	2.80

Table S2. Lowest vertical excitation energies ($S_0 \rightarrow S_1$), oscillator strengths (f) and molecular orbital compositions, computed at the TD-CAMB3LYP/6-31G* level of theory.

Compound	λ_{exc}	f	MO composition
monomer model	3.73 eV, 332 nm	1.320	HOMO \rightarrow LUMO (85%)
Polydiacetylene model	2.92 eV, 423 nm	1.087	HOMO \rightarrow LUMO (94%)

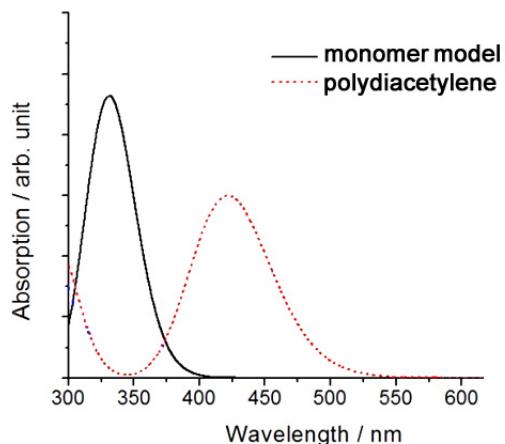


Figure S5. Simulated absorption spectra of the monomer model and polydiacetylene mode.

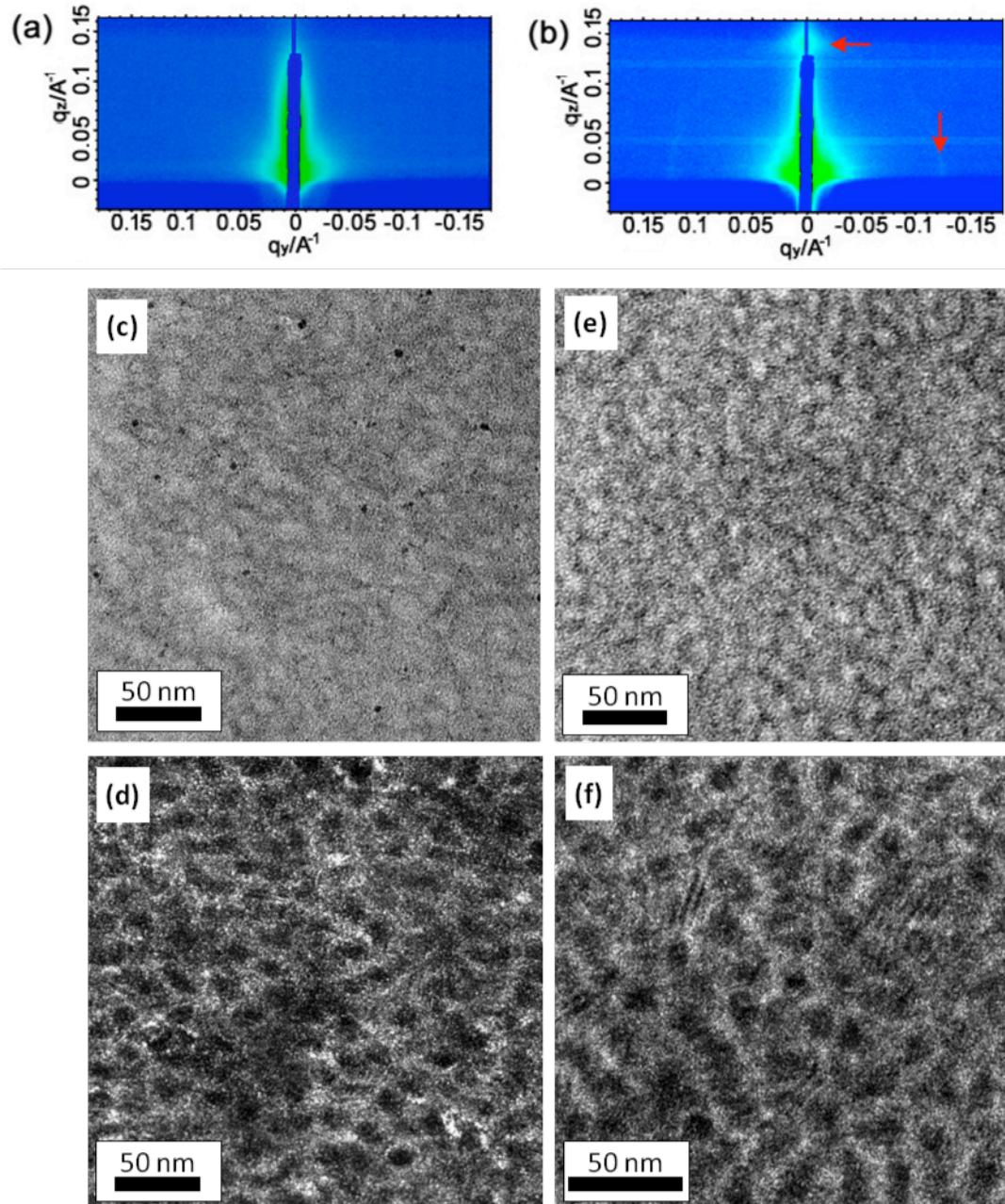


Figure S6. Grazing-incidence small angle X-ray scattering (GISAXS) data of PS-*b*-(PAA-sg-IDA_{R=0.4}): (a) as-cast film and (b) film after annealing in DMF. The peaks show local order, but long-range disorder, and the arrows point to the ring arising from local monomer order in the film. (c) Bright field TEM image and (d) HAADF-STEM image of an *as-cast* film of PS-*b*-(PAA-sg-IDA_{R=0.4}) after irradiation. (e) Bright field TEM and (f) HAADF-STEM images of an *annealed* of PS-*b*-(PAA-sg-IDA_{R=0.4}) after irradiation. Note: Figure S6f is a magnified region of Figure 4E, without the added dashed circles.

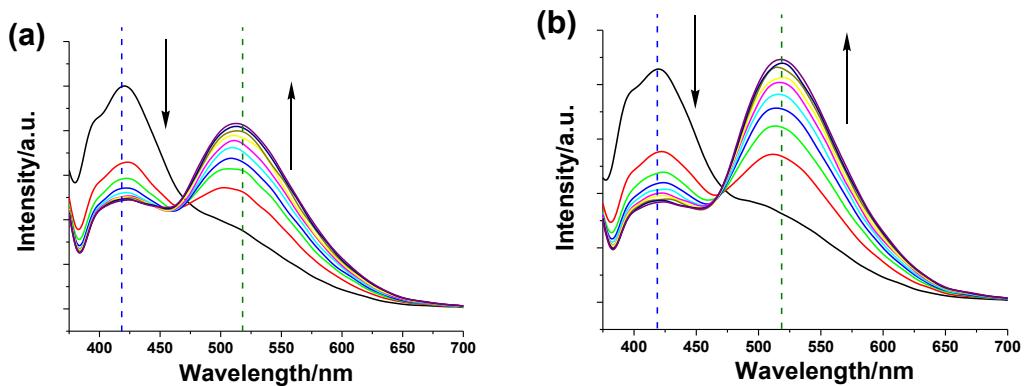


Figure S7. Emission spectra ($\lambda_{\text{ex}} = 365 \text{ nm}$) changes of (a) an as-cast film and (b) a film after solvent annealing with DMF vapor of PS-*b*-(PAA-*sg*-IDA_{R=0.2}). The spectra were recorded at various time intervals.

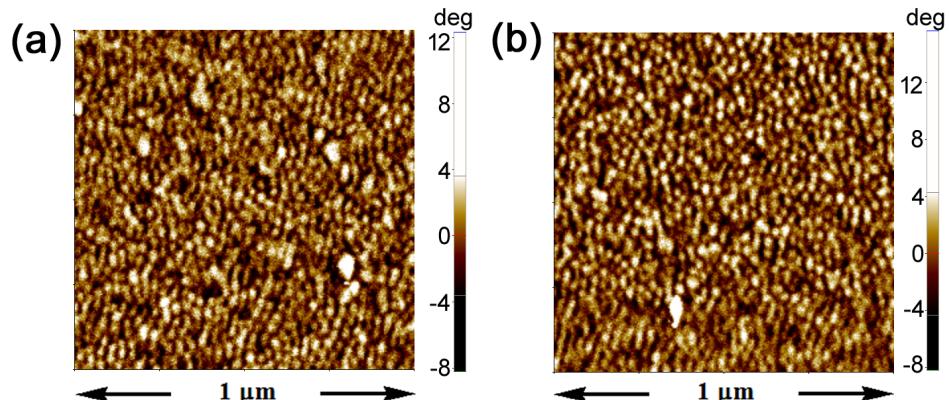


Figure S8. AFM (phase) images of P(S-*co*-BrS)-*b*-(PAA-*sg*-IDA_{R=0.2}) on (a) a film after solvent annealing with DMF vapor and (b) a micropatterned film after reannealing with DMF vapor.” It is missing a space after S8.

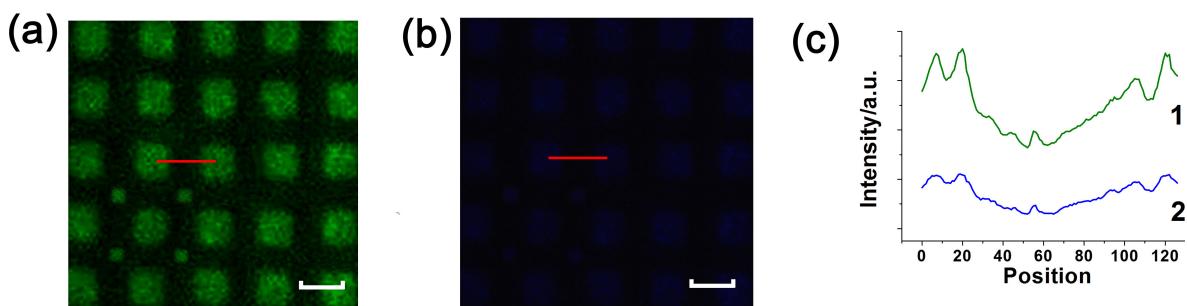


Figure S9. The confocal luminescence images for the patterning film after rinsing under the channel with the wavelength ranges of (a) 510–530 nm and (b) 460–480 nm. Scale bar, 500 μm. (c) (1,2) The intensity values of different channels (corresponding to the images (a) and (b), respectively) along the line highlighted.

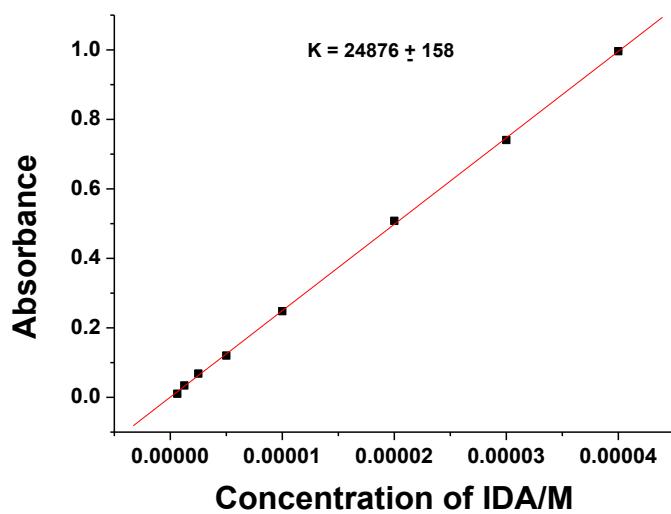


Figure S10. Plot of absorbance at 344 nm of the IDA monomer upon different concentrations.

Luminescence quantum yield was determined using optically matching solution of Rhodamine B ($\Phi_r = 0.7$) as standard.^{S1} The quantum yield was calculated using the below equation.

$$\Phi_s = \Phi_r (A_r F_s / A_s F_r) (\eta_s^2 \eta_r^2)$$

where, A_s and A_r are the absorbance of the sample and reference solutions, respectively, at the same excitation wavelength, F_s and F_r are the corresponding relative integrated fluorescence intensities, and η is the refractive index of the solvent. Accordingly, the quantum yield for IDA in this work is 6.79%.

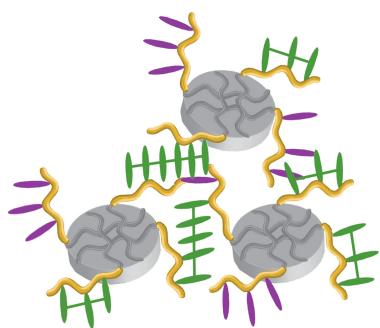


Figure S11. Proposed models of the PDA.

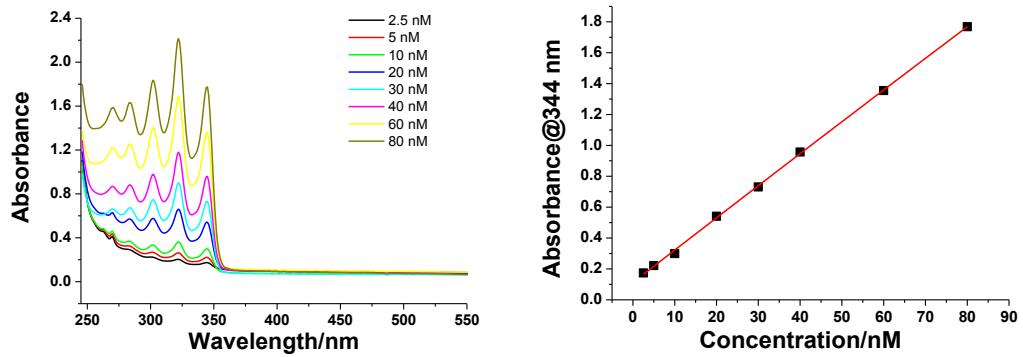


Figure S12. Absorption spectra of PS-*b*-P(AA-sg-IDA_{R=0.2}) with different concentrations (calculated by IDA) in chloroform. Plot of the absorption peak at 344 nm in PS-*b*-P(AA-sg-IDA_{R=0.2}) as a function of concentration.

REFERENCE

(S1) Kubin, R. F.; Fletcher, A. N. *J. Lumin.* **1982**, 27, 455.

NMR Spectra

