

Supporting Information

to

Cyclopolymerization-Derived Block-Copolymers of 4,4-Bis(octyloxymethyl)-1,6-heptadiyne with 4,4-Dipropargyl Malonodinitrile for Use in Photovoltaics

Mavila Sudheendran¹, Marta Horecha², Anton Kiriy^{2*}, Suren A. Gevorgyan³, Frederik C. Krebs³, Dongre Wang¹, and Michael R. Buchmeiser^{1,4*}

Table S1. Summary of cyclopolymerization results for **M1** using **I1- I3**.

| # | initiator | [M]/[I] | $M_n(\text{theor.})$ [g/mol] ^a | $M_n(\text{found})$ [g/mol] ^b | PDI | λ_{max} [nm] ^c | yield [%] ^d |
|---|-----------|---------|--|---|-----|---|---------------------------|
| 1 | I1 | 50 | 18800 | 52000 | 3.5 | 550 | 83 |
| 2 | I2 | 25 | 9400 | 12000 | 3.1 | 549 | 25 |
| 3 | I2 | 25 | 9400 | 63000 | 3.8 | 552 | 68 ^e |
| 4 | I3 | 25 | 9400 | 180000 | 3.4 | 549 | 34 |
| 5 | I3 | 50 | 18800 | 82000 | 3.2 | 550 | 84 |
| 6 | I3 | 25 | 9400 | 84000 | 4.2 | 550 | 56 ^e |

Polymerization conditions: 1,2-dichloroethane except for entries 1 and 5 (in THF), $T = 50^\circ\text{C}$

entries 1 and 5 at 0°C , $t = 24\text{h}$, ^aincluding end groups, ^bdetermined by SEC vs. PS standards,

^c in CHCl_3 , ^disolated yields, ^e initiator with 10 equiv. 3-Br-Py.

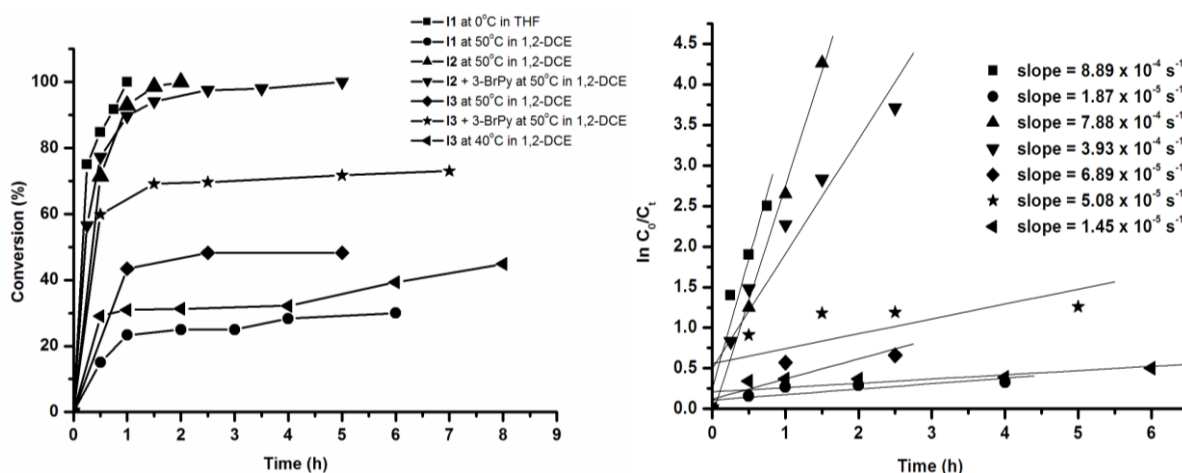


Figure S1. Kinetic plots obtained for the homopolymerization of **M1** using **I1-I3** at different reaction conditions. 1st-order plots (right)

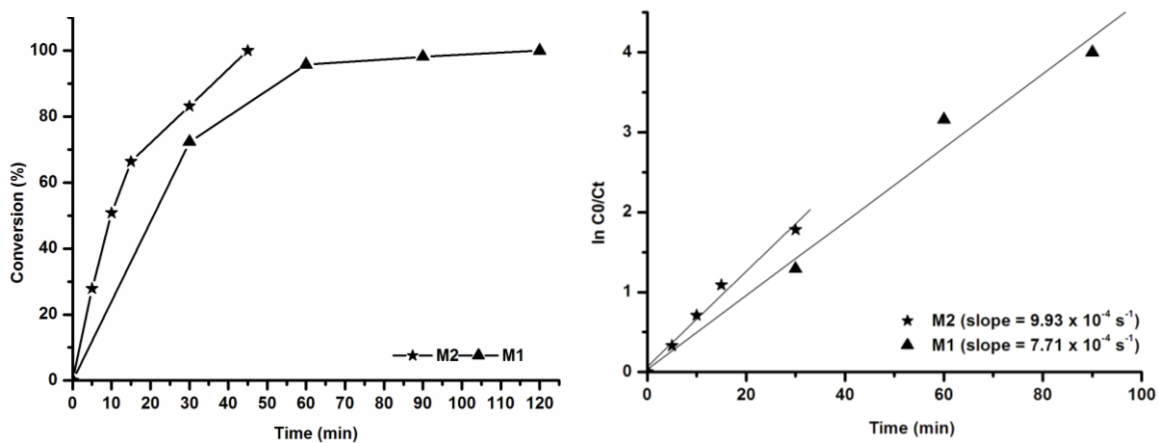


Figure S2. Kinetic plot obtained for the synthesis of poly(**M2**)-*b*-poly(**M1**) using **I4** (left), 1st order plot (right).

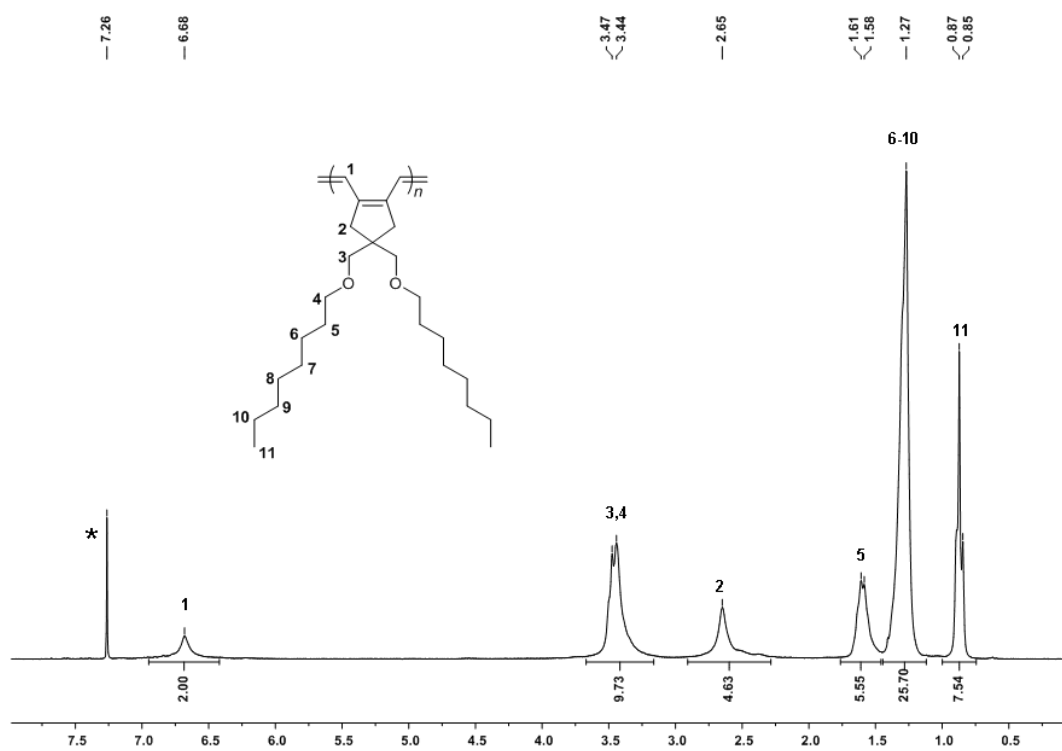


Figure S3. ¹H NMR spectrum of poly(**M1**)₂₅ synthesized by **I2** (*denotes CDCl₃).

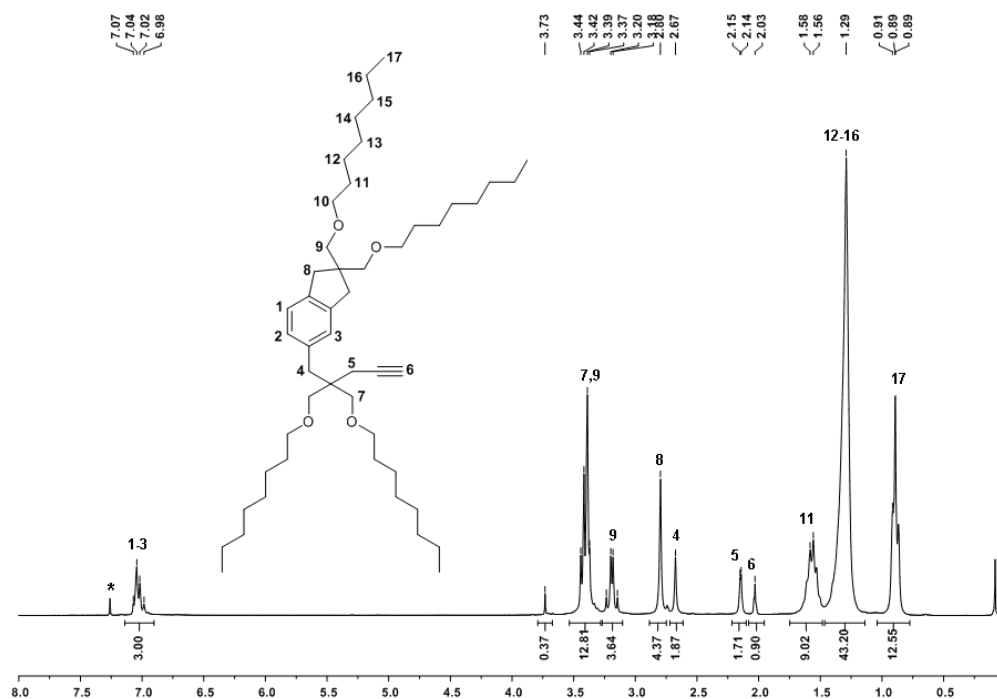


Figure S4. ¹H NMR spectrum of of the dimer 1 (*denotes CDCl₃).

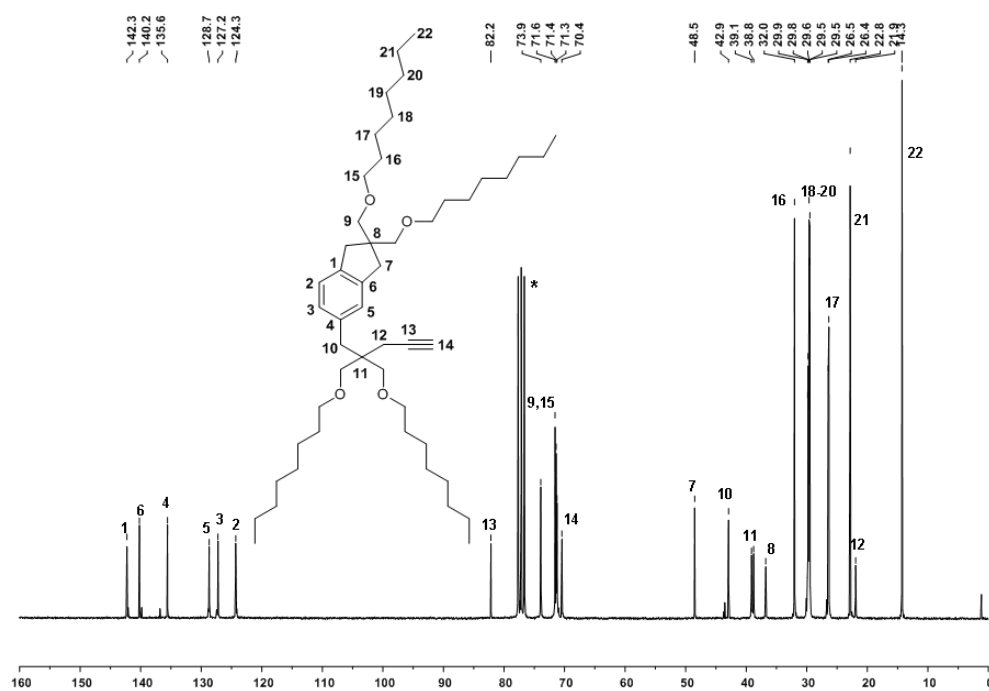


Figure S5. ¹³C NMR spectrum of the dimer 1 (*denotes CDCl₃).

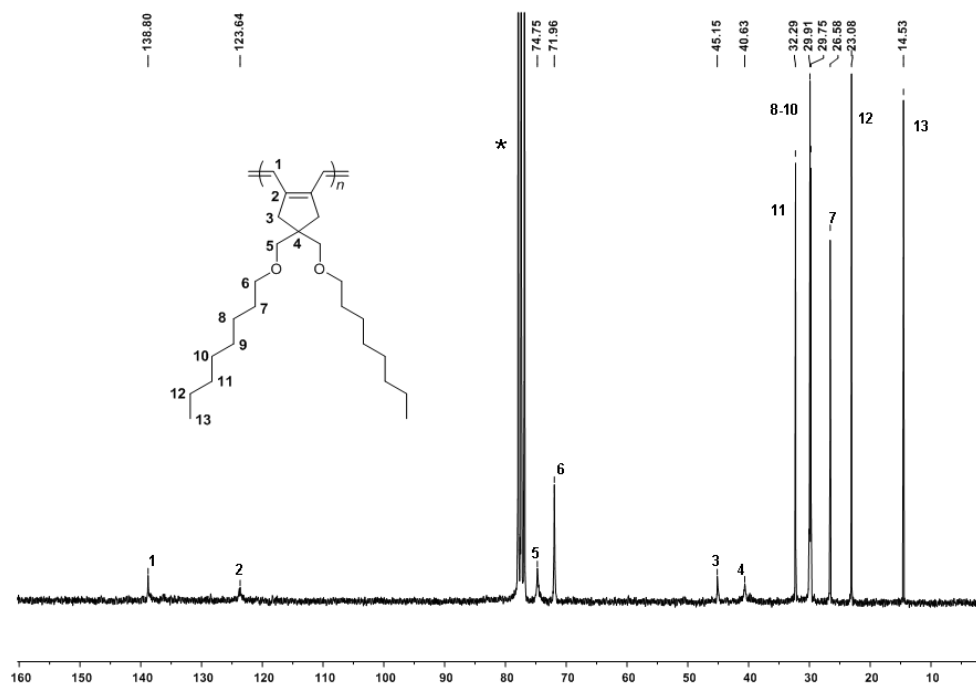


Figure S6. ^{13}C NMR spectrum of poly(M1)₂₅ synthesized by **I4** in presence of quinuclidine
(*denotes CDCl₃).

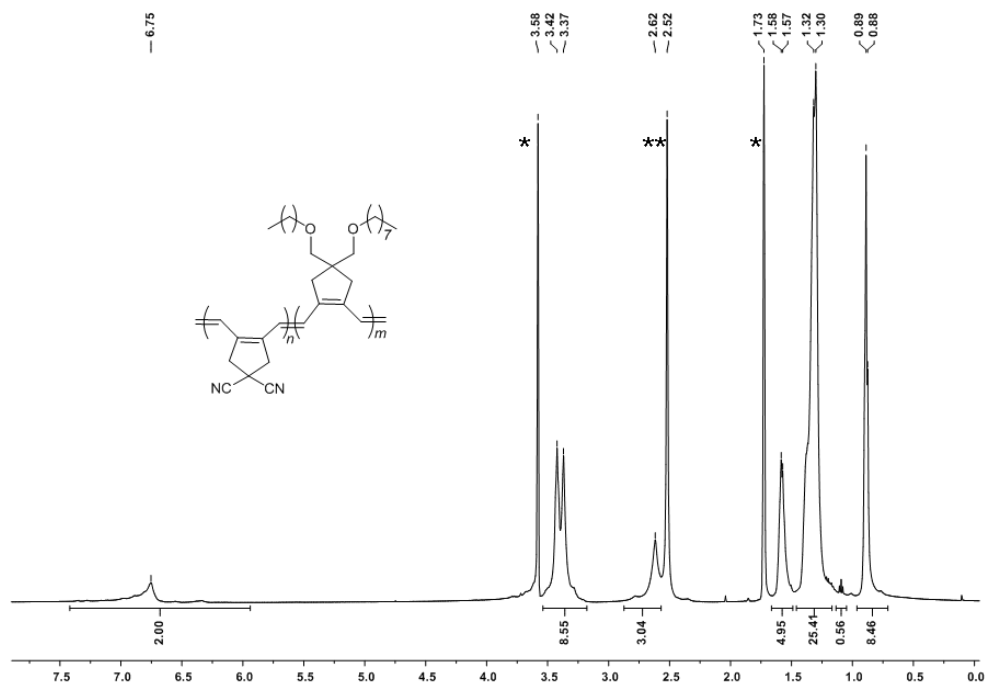


Figure S7. ^1H NMR spectrum of poly(M2)₁₅-b-poly(M1)₂₅ synthesized by **I4** in presence of quinuclidine (*denotes THF-*d*8 and **denotes water).

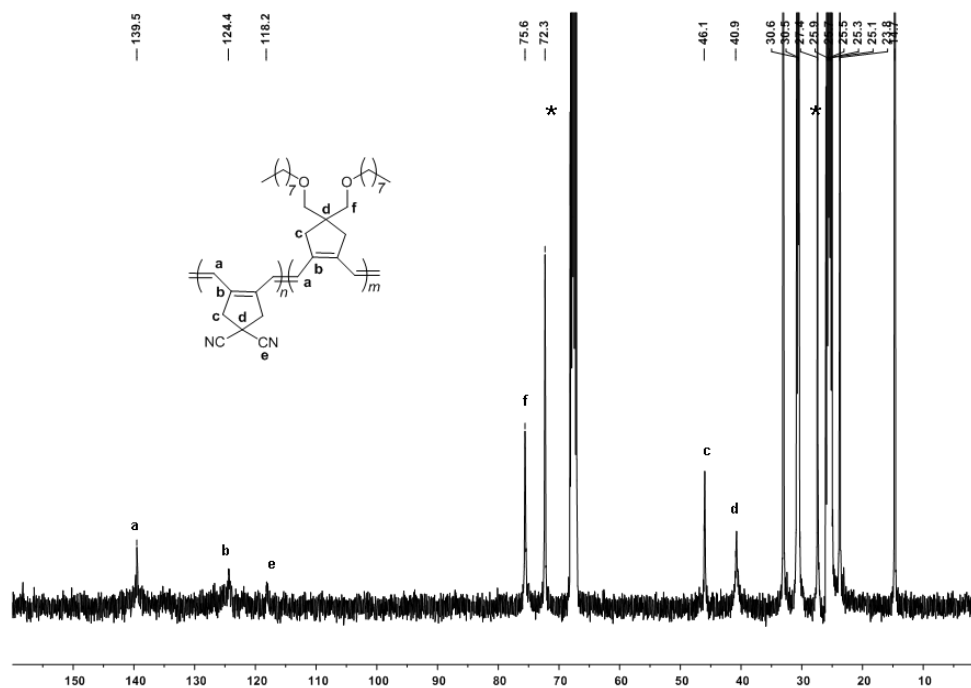


Figure S8. ¹³C NMR spectrum of poly(M2)₁₅-b-poly(M1)₂₅ synthesized by **I4** in the presence of quinuclidine (*denotes THF-*d*₈).

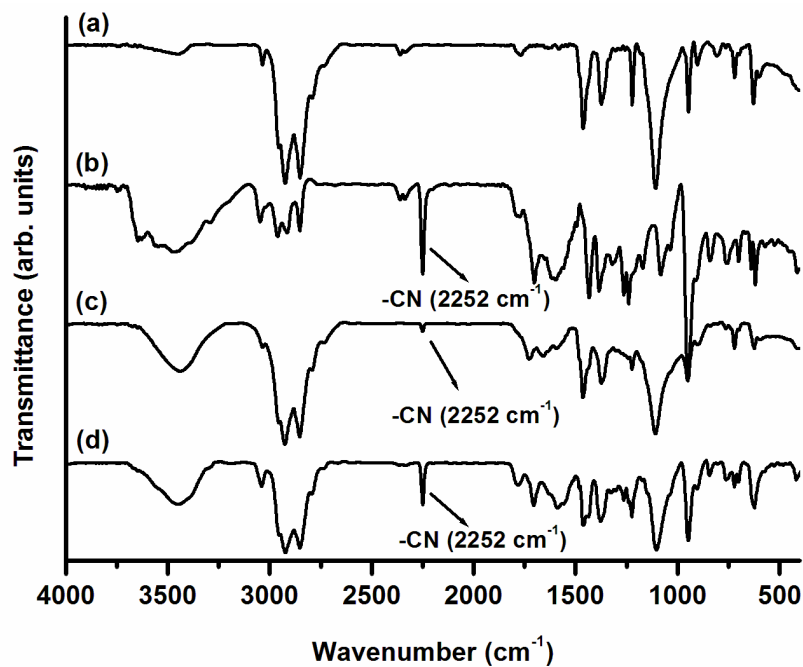


Figure S9. IR spectra (ATR mode) of the homo and block copolymers of **M1** and **M2**. (a) poly(M1), (b) poly(M2), (c) poly(M1)-b-poly(M2), (d) poly(M2)-b-poly(M1).

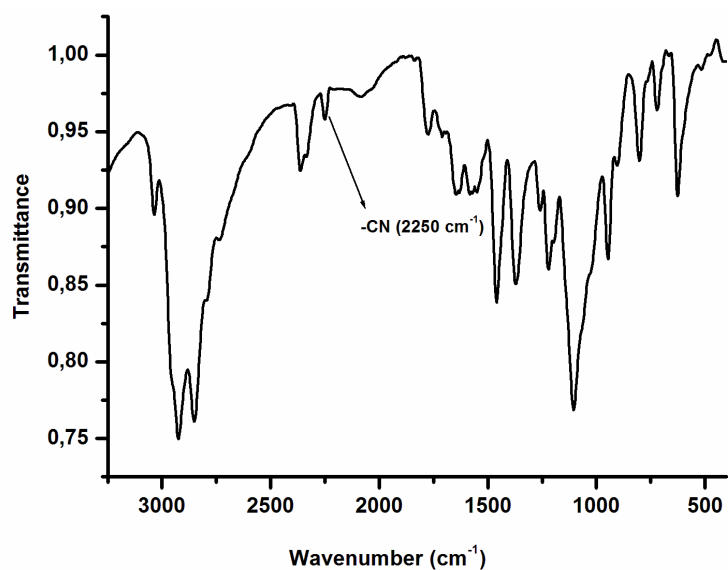


Figure S10. IR spectrum of telechelic poly(M2)-*b*-poly(M1) in the ATR mode.

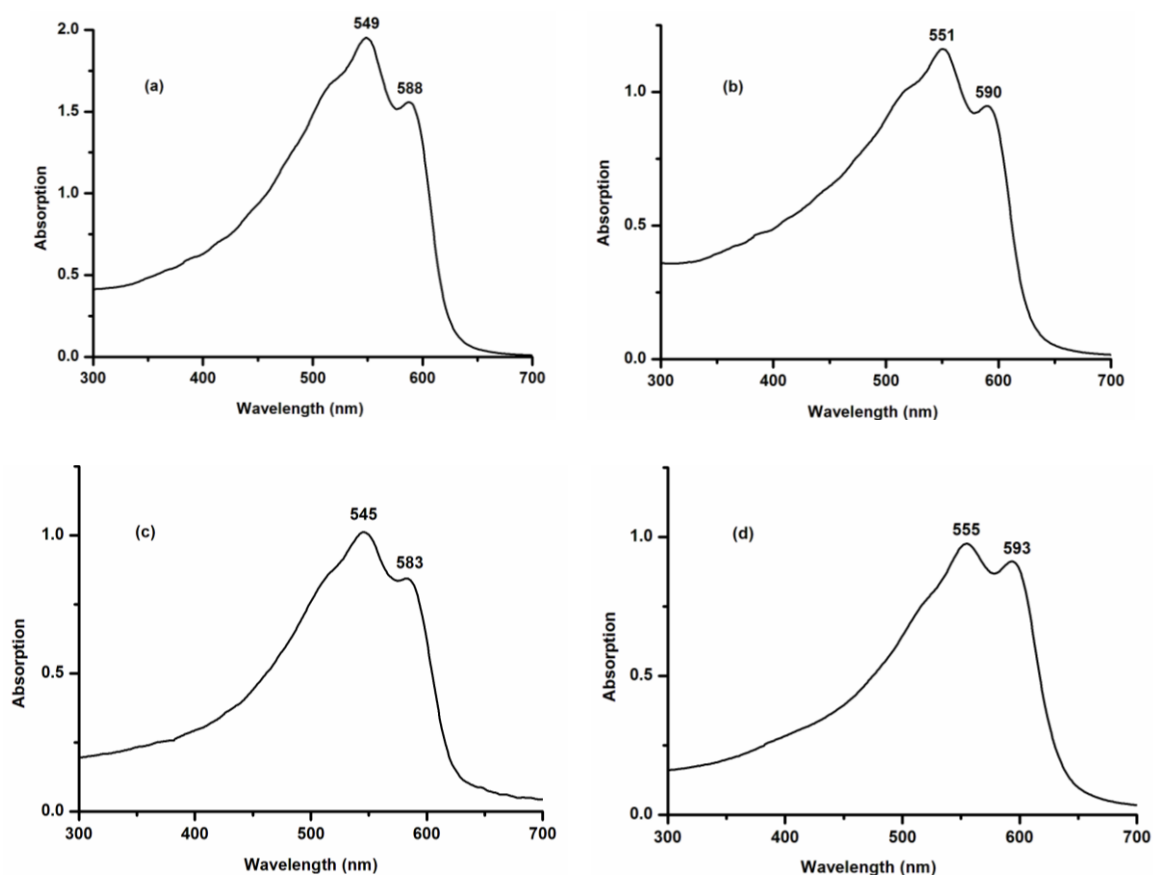


Figure S11. UV-vis spectra of the homo and block copolymers in CHCl₃. (a) poly(M1) prepared by **I2**, (b) poly(M1) prepared by **I4**, (c) poly(M1)-*b*-poly(M2) prepared by **I4**, (d) poly(M2)-*b*-poly(M1) prepared by **I4**.

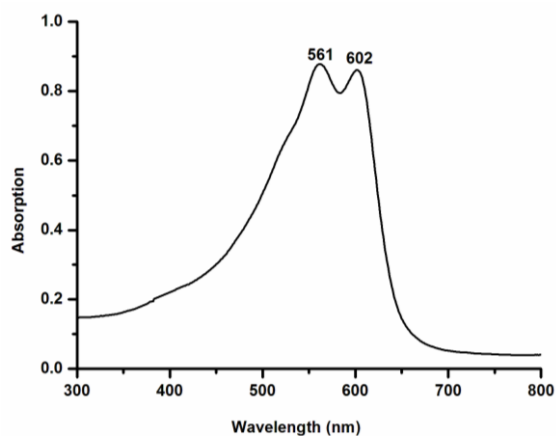


Figure S12. UV-vis spectra of telechelic poly(M2)-*b*-poly(M1) in CHCl₃.

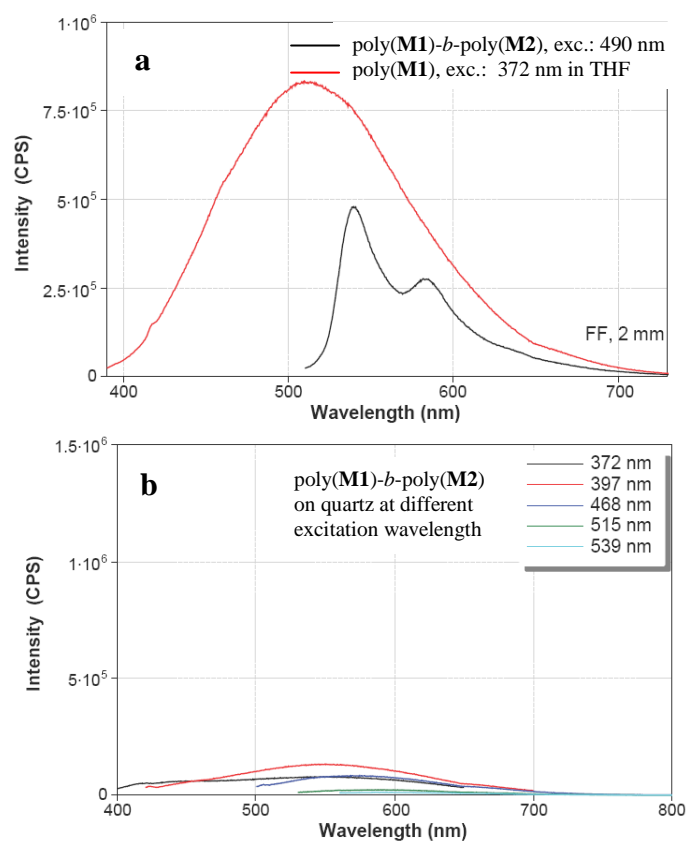


Figure S13. Emission spectra of poly(M1)-*b*-poly(M2) and poly(M1) in THF solution (a) and in thin films (b).

References

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