

SUPPORTING INFORMATION

Photo-responsive thermoelectric materials derived from fullerene-C₆₀-PEDOT hybrid polymers

Hui Zhou,^a Yun Zheng,^a Xizu Wang,^a Hui Ru Tan,^a and Jianwei Xu^{*ab}

^aInstitute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602, Republic of Singapore.

^bDepartment of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Republic of Singapore.

*Corresponding author: Jianwei Xu

Email address: jw-xu@imre.a-star.edu.sg

Mailing address: Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis, #08-03, Singapore 138634

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Experimental

General. All synthetic manipulations were carried out under an atmosphere of dry argon gas using standard vacuum-line Schlenk techniques. All solvents were degassed and purified before use according to standard literature methods. Diethyl ether, hexanes, tetrahydrofuran, and toluene were purchased from Aldrich Chemical Co. Inc. and distilled from sodium/benzophenone ketyl before use.

Instrumentation. Elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer for C, H, and N determination. UV-vis and fluorescence spectra were obtained using a Shimadzu UV3101PC UV-vis-NIR spectrophotometer and a Perkin-Elmer LS 50B luminescence spectrometer with a Xenon lamp as light source, respectively. Thermal analysis was performed on a Perkin-Elmer thermogravimetric analyzer (TGA 7) in nitrogen at a heating rate of 20 °C/min from room temperature to 900 °C.

Materials synthesis.

Compound 1. Compound **1** was prepared following the reported method.¹ Under argon atmosphere, the mixture of C₆₀ (180 mg, 0.25 mmol) and 4-bromoaniline (427.42 mg, 2.50 mmol) in toluene (100 mL) was stirred at 40 °C for 2 days. After removal of solvent, the solid was washed with CHCl₃, THF and methanol, offering compound **1** as a black solid (216.0 mg, yield 49%). ¹H NMR (400.13 MHz, Toluene-*d*₆): δ 7.12 (m, 2H), 6.59 (m, 2H), 6.05 (s, 1H). IR (thin film): ν = 3371, 2922, 2850, 2676, 2485, 1592, 1489, 1312, 1293, 1248, 1176, 1071, 1008, 821, 503 cm⁻¹. Anal. Calcd for C_{98.16}H_{38.16}Br_{6.36}N_{6.36}: C, 64.97; H, 2.12; Br, 28.00; N, 4.91. Found: C, 65.19; H, 2.21; Br, 27.94; N, 5.01.

Compound 2. Compound **2** was prepared following the reported method.² Under argon atmosphere, *n*-BuLi (2.5 M in *n*-hexane, 1.2 mL, 3.0 mmol) was slowly added to a solution of 3,3-didecyl-3,4-dihydro-2H-thieno[3,4-*b*][1,4]dioxepine (1.26 g, 2.88 mmol) in dry THF (30 mL) at -78 °C. The resulted reaction mixture was stirred at -78 °C for an additional 4 h, then a solution of tributyltin chloride in THF (0.777 mL, 2.88 mmol) was added. After slowly warmed to room temperature for overnight, the reaction mixture was quenched with dropwise addition of water (3.0 mL). The solvent was removed under reduced pressure, the residue was dissolved in DCM, which was washed with saturated NH₄Cl and dried over MgSO₄. Compound **2** was afforded after removal of DCM, which was used for next reaction without further purification.

Compound 3. Under argon atmosphere, the mixture of compound **1** (43.50 mg, 0.025 mmol), compound **2** (120.06 mg, 0.20 mmol), Pd(PPh₃)₄ (2.89 mg, 0.0025mmol) in anhydrous 1,2-dichlorobenzene (2.0 mL) was stirred at 80 °C for overnight. After cooling to room temperature, the reaction mixture was poured into CHCl₃. The solid was obtained by filtration, which was further washed with CHCl₃, THF and methanol, offering compound **3** as a dark brown solid (96.46 mg, yield 98%). ¹H NMR (400.13 MHz, CDCl₃): δ 6.98 (m, 2H), 6.64 (m, 2H), 6.45 (s, 1H), 3.96 (m, 4H), 1.27 (m, 36H), 0.87 (m, 6H). IR (thin film): ν = 3360, 1622, 1593, 1489, 1438, 1385, 1315, 1247, 1109, 1072, 1010, 818, 786, 752, 725, 693, 529 cm⁻¹. Anal. Calcd for C_{233.91}H_{279.31}N_{5.27}O_{10.54}S_{5.27}: C, 80.22; H, 8.04; N, 2.11; O, 4.81; S, 4.82. Found: C, 80.41; H, 8.19; N, 2.25; O, 5.05; S, 4.96.

Table S1. Feeding ratio, experimental ratio and thermal data of **HP1-7^a**.

Hybrid Polymers	Loading wt% of C ₆₀	Separation Yield (%)	T _d ^b (°C)
HP1	0	100	247
HP2	0.25	100	248
HP3	0.5	100	251
HP4	1.0	100	282
HP5	2.0	100	287
HP6	3.0	100	310
HP7	5.0	100	315

^bT_d: the decomposition temperature at which 5% weight loss occurs.

Organic components of C₆₀ based compounds determined by thermogravimetric analysis.

The organic components of compound **1** and **3** were analysed by thermogravimetric method, in which sample was heated from room temperature to 900 °C at a rate of 20 °C/min in nitrogen. The organic component covalently attached to C₆₀ would be lost at the decomposition temperature. As shown in Fig. S1, compound **1** and **3** show the decomposition temperature as 647 and 678 °C, respectively. The flat stages after decomposition temperature suggest the C₆₀ residue of compound **1** and **3**. Thus, the organic components of compound **1** and **3** would be calculated by equation 1 and 2, respectively.

$$\frac{x \times 170.97}{x \times 170.97 + 720.66} = 60.16\% \quad (\text{eq 1}) \quad x = 6.36$$

$$\frac{x \times 527.38}{x \times 527.38 + 720.66} = 80.01\% \quad (\text{eq 2}) \quad x = 5.47$$

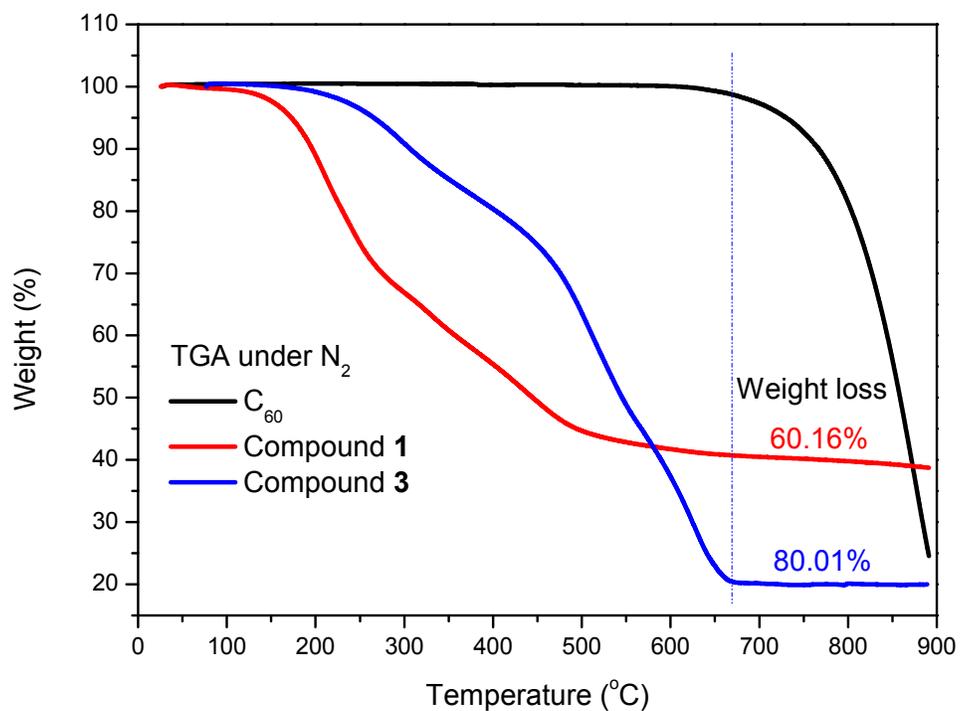


Fig. S1 Thermogravimetric analysis of C₆₀, compound 1 and compound 3.

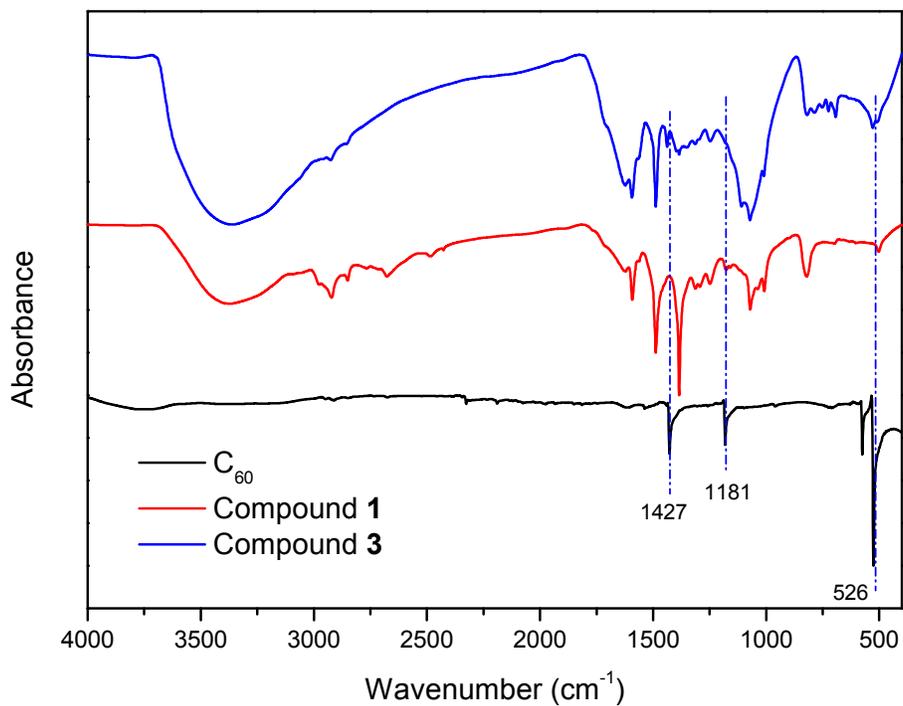


Fig. S2 FTIR of C₆₀, compound 1 and compound 3 in KBr.

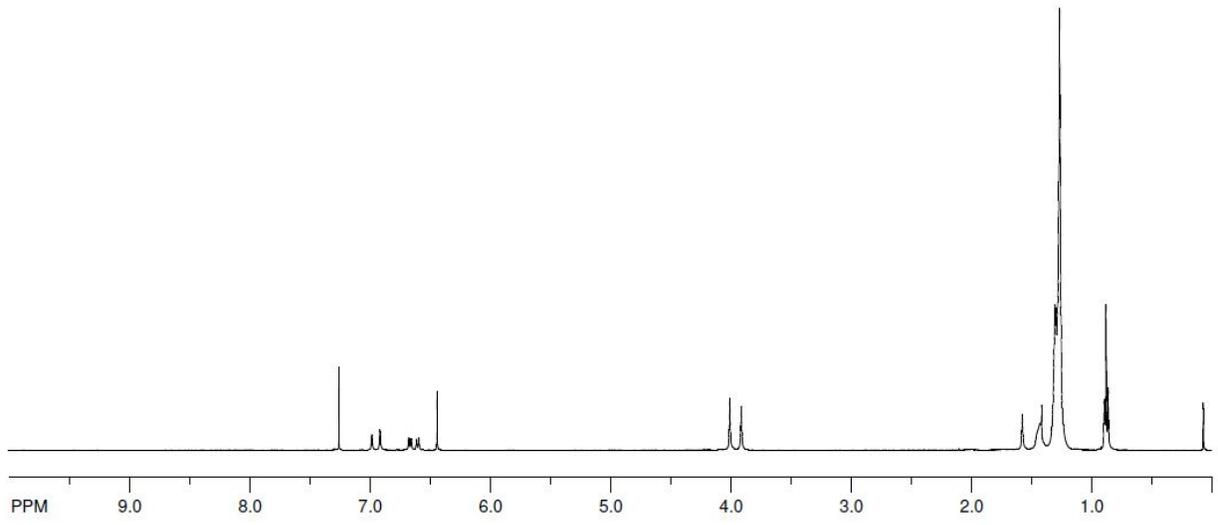


Fig. S3 ^1H NMR spectrum of compound **3**.

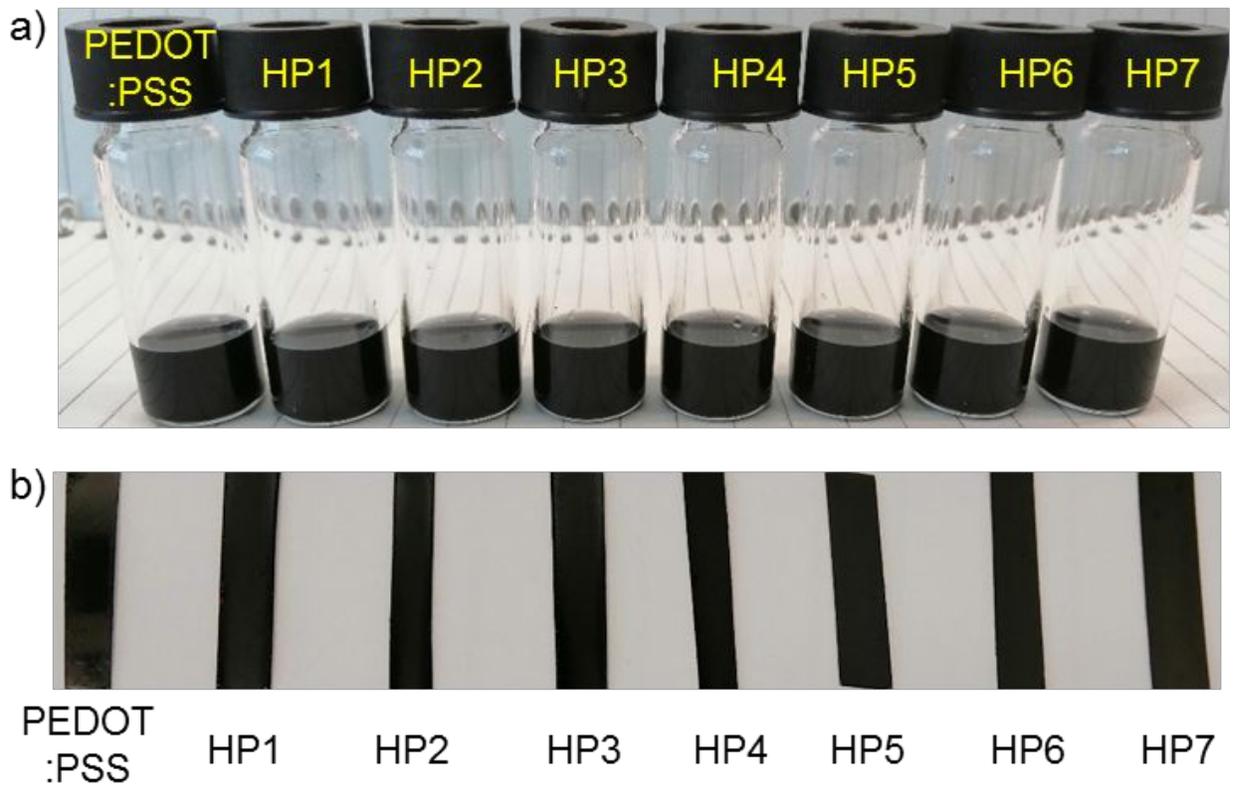


Fig. S4 (a) The photography of hybrid polymers **HP1-7** dispersion for film fabrication. (b) The photography of **HP1-7** films fabricated through drop casting from the solution of hybrid polymers.

The simulation of Pisarenko plot.

The dominant scattering mechanism of **HP1-7** is acoustic phonon scattering, so the scattering factor $r = -1/2$. The reduced Fermi energy η should be derived from the measured Seebeck coefficients,

$$S = \pm \frac{k_B}{e} \left(\frac{(r + 5/2)F_{r+3/2}(\eta)}{(r + 3/2)F_{r+1/2}(\eta)} - \eta \right) \quad (\text{eq 2})$$

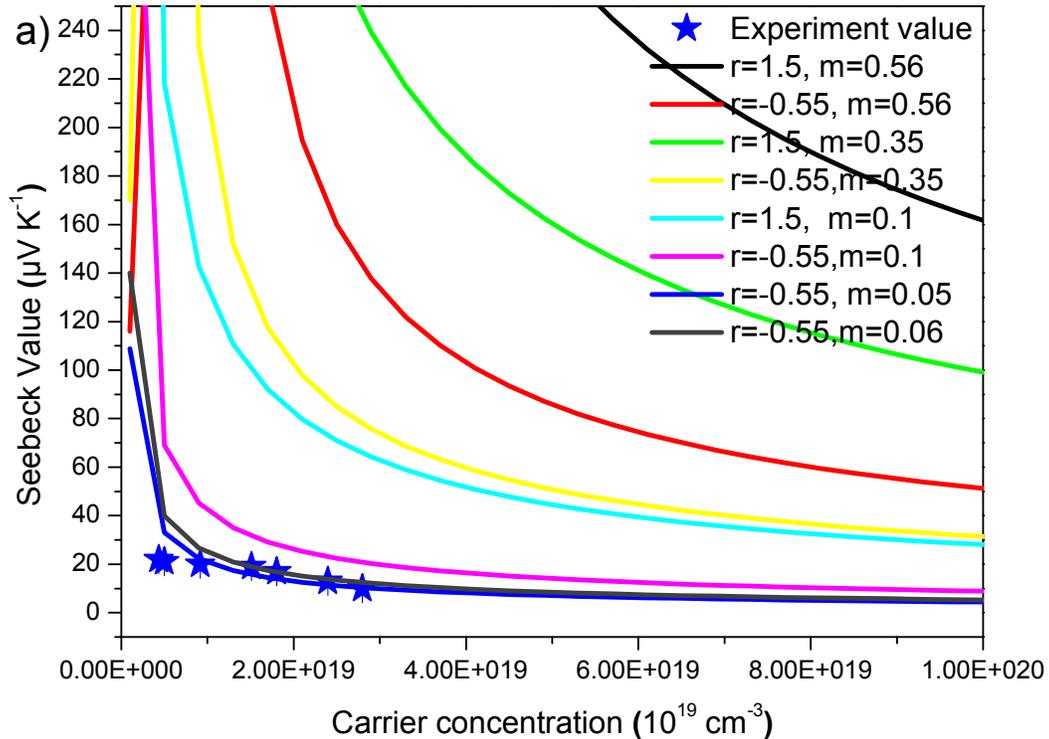
where $F_n(\eta)$ is the n^{th} -order Fermi integral,

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \eta}} d\chi \quad (\text{eq 3})$$

where k_B is the Boltzmann constant and e is the electron charge. The carrier effective mass (m^*) is calculated from,

$$m^* = \frac{h^2}{2k_B T} \left[\frac{n_e}{4\pi F_{1/2}(\eta)} \right]^{2/3} \quad (\text{eq 4})$$

where h is Plank constant and n_e is the carrier concentration.⁴ Based on the experimental data of S and n for fabricated **HP1-7** film, m^* was calculated to be $\sim 0.1 m_0$ (m_0 is the static mass of an electron). The experimental data and Pisarenko plot of Seebeck coefficient as a function of carrier concentration at room temperature were listed in Fig. S5.



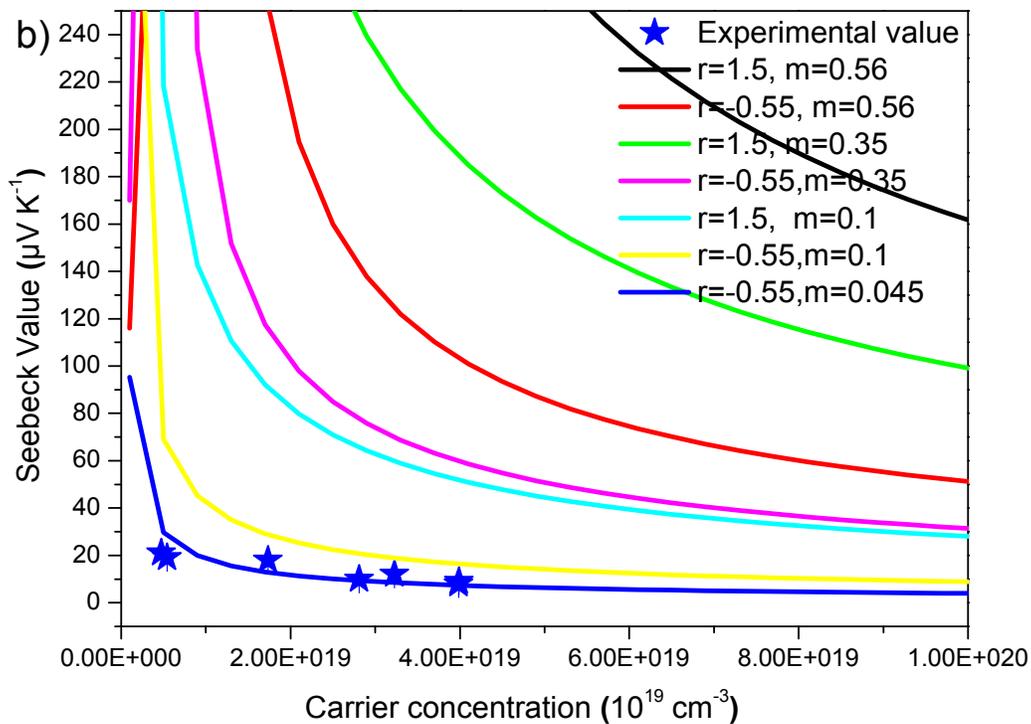


Fig. S5 (a) The Seebeck coefficient as a function of carrier concentration for **HP1-7** in dark condition. (b) The Seebeck coefficient as a function of carrier concentration for **HP1-7** under visible light irradiation.

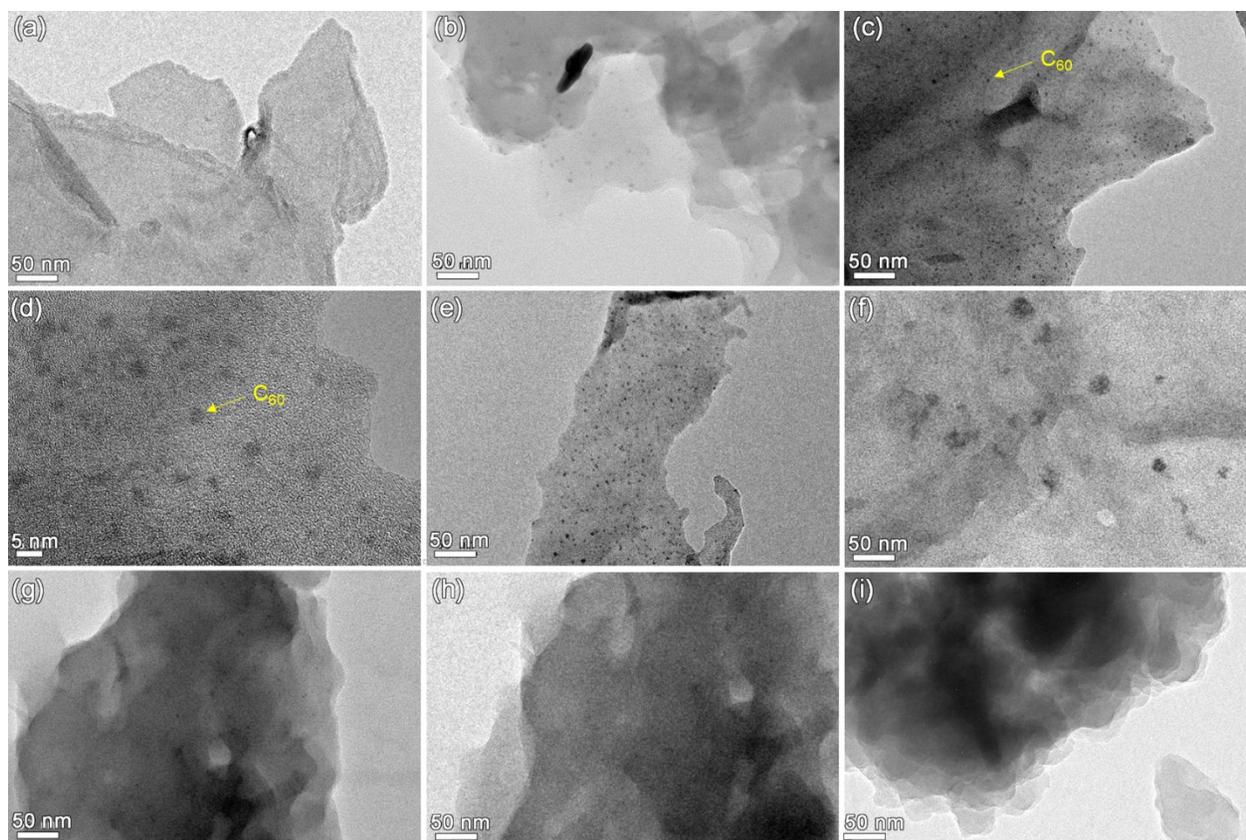


Fig. S6 TEM images of hybrid polymer composites with different weigh contents of C₆₀: (a) HP1; (b) HP2; (c) & (d) HP3; (e) HP3 under exposure in visible light irradiation for 1 month, (f) HP4; (g) HP5; (h) HP6; (i) HP7.

Reference

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