Three-Point Hydrogen Bonding Assembly between a Conjugated PPV and a Functionalized Fullerene

Hongjuan Fang,[†,‡] Shu Wang,[†] Shengqiang Xiao,[†,‡] Junlin Yang,[†] Yuliang Li,*[,†] Zhiqiang Shi,[†] Hongmei Li,[†,‡] Huibiao Liu,[†] Shengxiong Xiao,[†] and Daoben Zhu[‡]

Graduate School of Chinese Academy of Sciences, and Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

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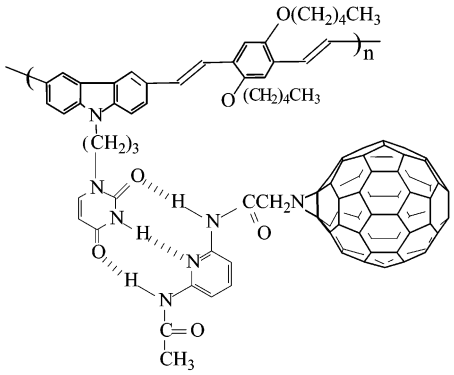
A new self-assembly system between a PPV derivative and an organofullerene through a three-point hydrogen-bonding interaction was prepared. The formation of hydrogen bonding was confirmed by ^{1}H NMR studies in $CDCl_3$. Fluorescence quenching experiments indicated that the fluorescence of U-PPV was greatly quenched by DAP-C_{60} ($K_{SV} = 5.8 \times 10^4$ M^{-1}).

Introduction

Since the discovery of photoinduced charge transfer in composites of π-conjugated polymers (electron donor) and [60]fullerene (electron acceptor),[1,2] the preparation of photovoltaic cells using the composites as the active layer has received much attention.[3−9] Significant improvement of the energy conversion efficiency of the cells has been achieved by blending the π-conjugated polymers and [60]fullerene and by creating a bulk heterojunction layer with a phase separation, interpenetrating network.[5,6] Besides blending the donor and acceptor together, supramolecular assembly is also a potential way to obtain bulk heterojunction material.[10−12] Hydrogen bonding is a very useful means of constructing the supramolecular system and has been used for the design of various molecular aggregates in solid state or in solution.[13−22] Meanwhile, energy and electron-transfer processes have also been investigated in some systems assembled through hydrogen bonding.[14,15,18,23,24]

Scheme 1. Structure of Self-assembly System of Derivated PPV with Fullerene by Three-Point Hydrogen Bonding



The formation of hydrogen bondings between groups of uracil and 2,6-diaminopyridine has proved to be an efficient way to construct supramolecular assembly.[13,17] In the present paper, two new compounds, U-PPV bearing uracil moiety (electron donor) and DAP-C_{60} containing a 2,6-diacylamidopyridine unit (electron acceptor), were designed and used to build a supramolecular system (Scheme 1) through a three-point hydrogen bonding.

Results and Discussion

The syntheses of the two key monomers U-PPV and DAP-C_{60} are sketched in Scheme 2 and Scheme 3,

* To whom correspondence should be addressed. E-mail: ylli@mail.iccas.ac.cn.

† Graduate School of Chinese Academy of Sciences.

‡ Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences.

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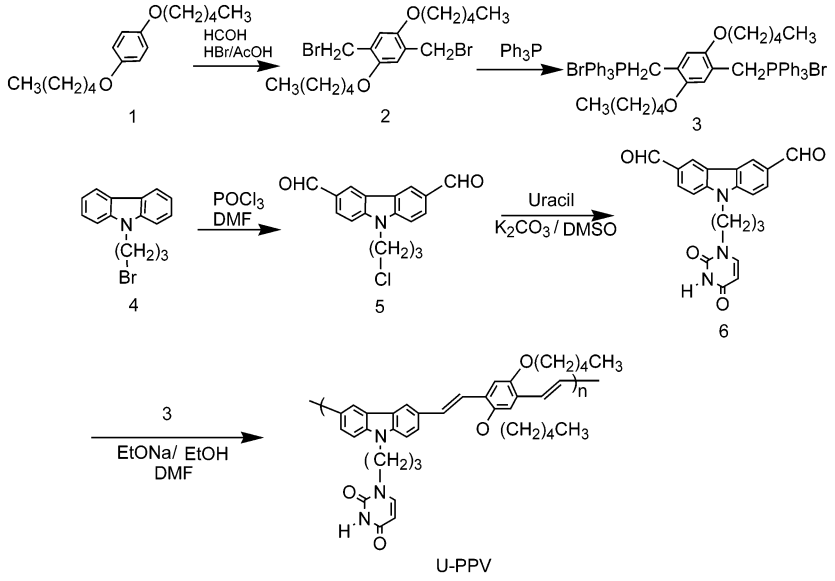
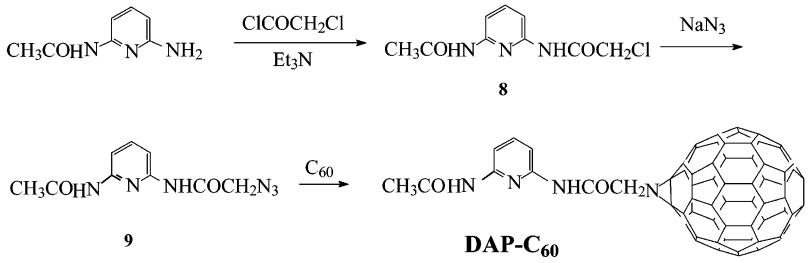
Scheme 2. Synthetic Route of the U-PPV



Scheme 3. Synthetic Route of the DAP-C_{60}



respectively. Briefly, U-PPV was prepared by Wittig condensation of 1,4-bis (triphenylphosphoniummethyl)-2,5-bis(pentoxy)-benzene dibromide **3** with *N*-(3-uracil-propyl)-3,6-diformyl-carbazole **6** under sodium ethoxide in *N*,*N*-dimethylformamide (DMF). DAP-C_{60} was prepared by reaction of 2-acetylamido-6-(2-azido-acetyl-amido)-pyridine **9** and 1 equiv. of C_{60} in chlorobenzene at reflux, which relied on the cycloaddition reaction of the azide group with C_{60}, pioneered by the Wudl group.[25,26]

The addition of azides to C_{60} in this reaction proceeded via intermediate triazolines, which rearranged to open 1,6-aza-bridged isomers and closed 1,2-aza-bridged isomers as major monoaddtion products after extrusion of N_2. With high symmetry, the closed 1,2-aza-bridged isomer obtained in the present reaction kept the framework of C_{60} better, which can be confirmed with the ^{13}C NMR spectrum. Except for two sp^3-C that appeared at δ 83.22 ppm, all other sp^2-C of C_{60} appeared at a narrow region of δ 149 to 140 ppm.

The U-PPV was easily soluble in common organic solvents, e.g., chloroform and THF. The DAP-C_{60} was only partially soluble in $CHCl_3$ and THF. The molecular weight of U-PPV was determined with an instrument of PL-GPC-210 using polystyrene as standard. The weight-average molecular weight (M_w) was 3440 and the polydispersity index was 1.97. The thermal property of

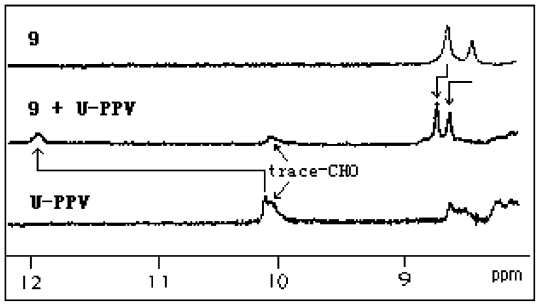


Figure 1. Partial ^1H NMR spectra of compound **9**, U-PPV, and (**9** + U-PPV) in $CDCl_3$; the concentration of each compound is 5 mM.

U-PPV was investigated by thermal gravimetric analysis (TGA), which showed good thermal stability up to 400 °C and obvious weight loss from 410 to 500 °C. The glass transition temperature (T_g) at 109.3 °C was determined by differential scanning calorimetry (DSC).

Evidence for the formation of self-assembly in $CDCl_3$ came from ^1H NMR spectroscopic studies. We first studied the formation of self-assembly of U-PPV and compound **9** without C_{60} moiety. Figure 1 shows the partial ^1H NMR spectra of U-PPV (5.0×10^{-3} M), compound **9** (5.0×10^{-3} M), and (U-PPV + **9**) (5.0×10^{-3} M, respectively) in $CDCl_3$. The singlets observed for compound **9** at δ 8.42 and δ 8.60 ppm are assigned to the two amidic protons, respectively. The singlet observed for U-PPV at δ 10.05 ppm is assigned to the imidic proton of uracil ring. While compound **9** was mixed with 1 equiv. of U-PPV in $CDCl_3$, marked downfield shifts were found for proton resonances of the

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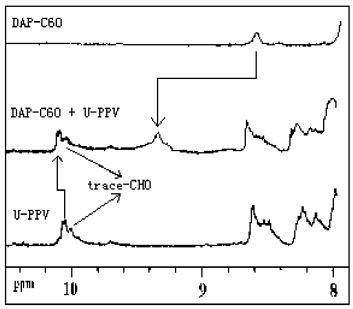

Figure 2. Partial ^{1}H NMR spectra of DAP-C_{60}, U-PPV, and (DAP-C_{60} + U-PPV) in $CDCl_3$; the concentration of each compound is 5 mM.

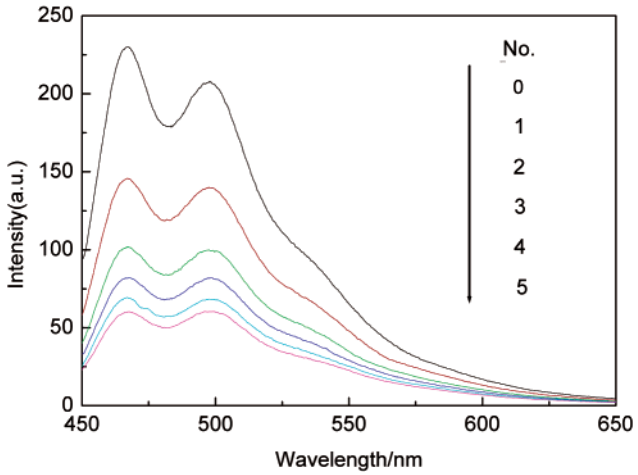

Figure 3. Fluorescence of U-PPV solution (1.0×10^{-5}M) in $CHCl_3$ quenched by DAP-C_{60} solution in $CHCl_3$ ($\lambda_{ex} = 430$ nm). The concentrations of DAP-C_{60} are 0, 0 M; 1, 1.0×10^{-5} M; 2, 2.0×10^{-5} M; 3, 3.0×10^{-5} M; 4, 4.0×10^{-5} M.

two amidic protons of compound **9** (from δ 8.42 and δ 8.60 to δ 8.62 and δ 8.75 ppm, respectively) and the imidic proton of uracil ring in U-PPV (from δ 10.05 to δ 11.95 ppm). These shifts showed that hydrogen bonding took place between the U-PPV and compound **9**. The changes are characteristic of the formation of a three-point hydrogen bonding complex.[13]

The assembly of U-PPV and DAP-C_{60} was also studied by ^{1}H NMR spectroscopy. Figure 2 is the partial ^{1}H NMR spectra of U-PPV (5.0×10^{-3} M), DAP-C_{60} (5.0×10^{-3} M), and (U-PPV + DAP-C_{60}) (5.0×10^{-3} M, 5.0×10^{-3} M, respectively) in $CDCl_3$. While DAP-C_{60} was blended with U-PPV, marked downfield shifts were also found for proton resonance of the amidic protons of DAP-C_{60} (from δ 8.61 to δ 9.35 ppm) and the imidic proton of uracil ring in U-PPV (from δ 10.05 to δ 10.15 ppm). These shifts also showed the formation of the supramolecular system between U-PPV and DAP-C_{60}.

A fluorescence quenching experiment of mixed U-PPV and DAP-C_{60} was carried out as shown in Figure 3. For comparison, a quenching experiment of *N*-methylpyrrolidino[60]fullerene (MPYLD-C_{60}) without forming hydrogen bond with U-PPV was also performed. Keeping the concentration of U-PPV unchanged, the concentrations of DAP-C_{60} or MPYLD-C_{60} were increased gradually. Because of the competition absorptions of DAP-C_{60} or MPYLD-C_{60} at the excitation and emission wavelength of U-PPV, the fluorescence intensities were

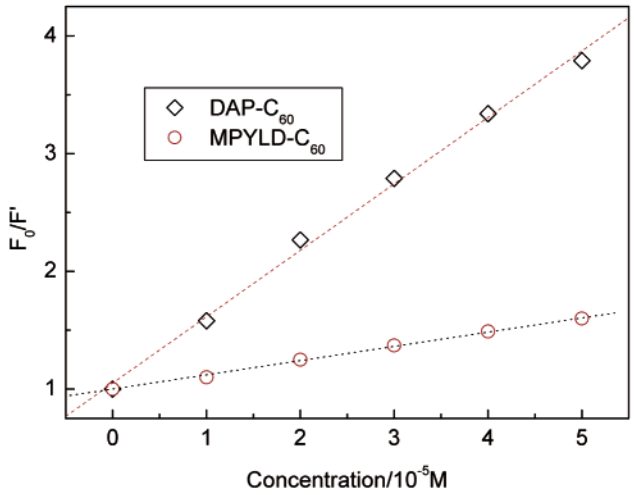

Figure 4. Dependence of F_0/F' on the concentration of DAP-C_{60} or MPYLD-C_{60}.

calibrated according to a literature method.[27] The quenching follows the Stern−Volmer equation

$$\frac{F_0}{F'} = 1 + K_{SV}[Q] \qquad (1)$$

where F_0 is the fluorescence intensity of U-PPV without addition of DAP-C_{60} or MPYLD-C_{60}, F' is the calibrated fluorescence intensity of U-PPV upon addition of DAP-C_{60} or MPYLD-C_{60}, K_{SV} is the quenching constant, and [*Q*] is the concentration of DAP-C_{60} or MPYLD-C_{60}.

Figure 4 demonstrates the dependence of relative fluorescence intensity (F_0/F') on the concentration of DAP-C_{60} or MPYLD-C_{60}. The results indicated that the fluorescence of U-PPV was quenched by DAP-C_{60} and MPYLD-C_{60}. The Stern−Volmer constant (K_{SV}) of DAP-C_{60} (5.8×10^4 M^{-1}) is much larger than that of MPYLD-C_{60} (1.2×10^4 M^{-1}), suggesting that the interaction between DAP-C_{60} and U-PPV is stronger than that between MPYLD-C_{60} and U-PPV owing to the formation of hydrogen bonds between U-PPV and DAP-C_{60}. Moreover, the fluorescence lifetimes (τ) of U-PPV with increasing concentration of DAP-C_{60} or MPYLD-C_{60} were measured by a single photon timing apparatus with excitation at 430 nm, monitored at 490 nm. At both wavelengths the absorption of DAP-C_{60} or MPYLD-C_{60} was very low. The fluorescence decay curve was well-fitted as a single exponential. The fluorescence lifetime of U-PPV in the absence of DAP-C_{60} or MPYLD-C_{60} (τ_0) was 1.05 ns. The dependence of τ/τ_0 on the concentration of DAP-C_{60} shown in Figure 5 indicated that the fluorescence lifetime of U-PPV did not change remarkably after addition of DAP-C_{60}. This fact displayed that the fluorescence quenching was static by the formation of the hydrogen bonds, which was consistent with the results of ^{1}H NMR studies. The K_{sv} constant would be identical to the equilibrium constant of the complex formed between U-PPV and DAP-C_{60}. The relatively large K_{sv} value reflected that the binding force through the hydrogen link was strong. It is worth mention that the K_{sv} constant derived from steady-state does not appear to be very reliable because the constant value

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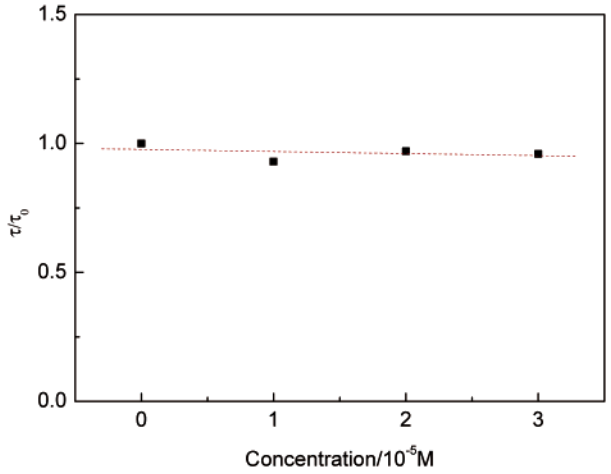

Figure 5. Dependence of τ/τ_0 on the concentration of DAP-C_{60}.

of the original equation was obtained based on several assumptions.[28] However, the fluorescence lifetime of U-PPV with increasing concentration of MPYLD-C_{60} decreased remarkably, indicating that the fluorescence quenching was dynamic in this case. The lifetime of the U-PPV in the presence of MPYLD-C_{60} (10^{-5} M) decreased to 0.90 ns. Because the time resolution of our apparatus is 200 ps, it is quite difficult to resolve the lifetimes of several hundreds of ps species (i.e., the concentrations of MPYLD-C_{60} is further increased). Further work is in progress.

Conclusion

The present paper outlines the synthesis of U-PPV bearing uracil moiety and DAP-C_{60} containing 2,6-diacylamidopyridine moiety and the construction of the supramolecular system through a three-point hydrogen-bonding interaction between them. Fluorescence quenching experiments indicate the presence of a strong interaction between U-PPV and DAP-C_{60} ($K_{SV} = 5.8 \times 10^4$ M^{-1}). Current efforts are focused on the studies of photoinduced charge transfer within this system and the construction of photovoltaic devices.

Experimental Section

Materials and Measurements. 1,4-Dipentyloxybenzene **1**,[29] *N*- (3-bromopropyl)-carbazole **4**,[30] and 2-amino-6-acetylamidopyridine **7**[31] were prepared according to literature procedures. All solvents were redistilled before use. NMR spectra were collected on either Bruker Avance DPS-400 (400 MHz) or Varian XL-200 (200 MHz) spectrometers. Mass spectra were obtained on a Bruker BIFLEXIII spectrometer. FTIR spectra were measured on a Bruker EQUINOX55 spectrometer. The fluorescence spectra were obtained on a Hitachi F-4500 spectrometer. Gel permeation chromatography (GPC) analyses were conducted with a PL-GPC-210 system using polystyrene as the standard and THF as the eluent. TGA and DSC were carried out using a Perkin-Elmer 7 series thermal analysis system.

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1,4-Bis(bromomethyl)-2,5-bis(pentoxy)-benzene (2). To a mixture of compound **1** (3.8 g, 15.1 mmol) and paraformaldehyde (0.93 g, 31 mmol) in 50 mL of acetic acid, 33 wt % HBr in acetic acid (5.5 mL, 32.2 mmol) was added dropwise under stirring. Subsequently, the mixture was stirred at 60−70 °C for 2 h, and then cooled to room temperature. The resulting solution was poured into 400 mL of H_2O, and a saturated solution of K_2CO_3 was added to adjust the pH value in the range of 5 to 6. After the solution was filtered, washed with H_2O, and recrystallized from EtOH, a slightly yellow crystal of 5.03 g was obtained (76.0%). Mp 79−80 °C. FTIR (KBr pellet, cm^{-1}): 2953, 2930, 2870, 1511, 1230. ^{1}H NMR ($CDCl_3$, ppm) δ: 6.85 (s, 2H), 4.53 (s, 4H), 3.98 (t, J = 7.21 Hz, 4H), l.81 (m, 4H), l.47 (m, 4H), 1.36 (m, 4H), 0.93 (t, J = 7.26 Hz, 6H). MS (EI): 434(M). Anal. Calcd for $C_{18}H_{28}Br_2O_2$: C, 49.56; H, 6.47. Found: C, 49.57; H, 6.55%.

1,4-Bis(triphenylphosphoniummethyl)-2,5-bis(pentoxy)-benzene dibromide (3). A solution of 325.5 mg (0.75 mmol) of compound **2** and 393 mg (1.5 mmol) of PPh_3 in 10 mL of toluene was refluxed for 6 h. The precipitate formed was filtered off and dried at vacuum at room temperature for 6 h to give 567 mg of white powder (78.9%). FTIR (KBr pellet, cm^{-1}): 2951, 2864, 1510, 1437, 1220, 1111. ^{1}H NMR ($CDCl_3$, ppm): δ 7.57−7.78 (br, 32H), 5.21 (d, J = 12.15 Hz, 4H), 2.98 (t, J = 5.13 Hz, 4H), l.02−1.21 (m, 12H), 0.82 (t, J = 7.26 Hz, 6H). MS (MALDI-TOF): 798 (M-2Br). Anal. Calcd for $C_{54}H_{58}Br_2P_2O_2 \cdot 2H_2O$: C, 66.80; H, 6.02. Found: C, 66.76; H, 5.79%.

***N*-(3-Chloropropyl)-3,6-diformyl-carbazole (5).** To 19.1 g (0.26 mol) of *N*,*N*-dimethylformamide cooled to 0 °C, 19.8 g (0.13 mol) of phosphoryl chloride was added dropwise, and then the mixture was kept at room temperature to react for 1 h. To the stirred mixture, l.92 g (6.7 mmol) of *N*-(3-bromopropyl)-carbazole (**4**) was added. After standing for 36 h at 90 °C, the mixture was poured into l50 mL of water and the precipitate was filtered off. The crude product was recrystallized from chloroform/*n*-hexane to give a yellow powder of 1.0 g, yield 50.0%. FTIR (KBr pellet, cm^{-1}): 2961 2821, 1683,1593, 1488. ^{1}H NMR ($CDCl_3$, ppm): δ 10.17 (s, 2H), 8.72 (s, 2H), 8.12 (d, J = 8.37 Hz, 2H), 7.66 (d, J = 8.58 Hz, 2H), 4.63 (t, J = 6.60 Hz, 2H), 3.55 (q, J = 5.67 Hz, 2H), 2.38 (m, 2H). MS (EI): 299-(M). Anal. Calcd for $C_{17}H_{14}ClNO_2 \cdot 0.33H_2O$: C, 66.78; H, 4.81; N, 4.58. Found: C, 66.79; H, 4.48; N, 4.38%.

***N*-(3-Uracil-propyl)-3,6-diformyl-carbazole (6).** A solution of 59.8 mg (0.2 mmol) of compound **5**, 67.2 mg (0.6 mmol) of uracil, 30.0 mg (0.2 mmol) of NaI, and 82.8 mg (0.6 mmol) of K_2CO_3 in 5 mL of DMSO was reacted at 90 °C for 6 h and then cooled to room temperature. The resulting solution was poured into 30 mL of H_2O. After the solution was filtered, washed with H_2O, and dried under vacuum, a yellow solid of 20.2 mg was obtained (26.9%). ^{1}H NMR (DMSO-d_6, ppm): δ 11.20 (s, 1H), 10.11 (s, 2H), 8.92 (s, 2H), 8.10 (d, J = 8.45 Hz, 2H), 7.88 (d, J = 8.45 Hz 2H), 7.60 (d, J = 8.20 Hz, 1H), 5.51 (d, J = 8.20 Hz, 1H), 4.59 (q, 2H), 3.80 (q, 2H), 2.11 (m, 2H). ^{13}C NMR (DMSO-d_6, ppm): δ 192.3, 164.1, 151.9, 145.6, 144.5, 129.7, 127.7, 124.7, 122.8, 110.9, 101.4, 45.6, 38.7, 28.2. MS (EI): 375(M). Anal. Calcd for $C_{21}H_{17}N_3O_4$: C, 67.19; H, 4.56; N, 4.58. Found: C, 67.10; H, 4.52; N, 4.50%.

2-Acetylamido-6-(2-chloro-acetylamido)-pyridine (8). To a solution of 0.35 g (2.3 mmol) of 2-amino-6-acetylamidopyridine in 20 mL of dried CH_2Cl_2, 0.18 mL (2.3 mmol) of 2-chloro-acetyl chloride were added dropwise during 20 min, and then the mixture was kept at room temperature to react for 2 h. The resulting solution was poured into 20 mL of saturated aqueous Na_2CO_3 solution, and then the CH_2Cl_2 layer was transferred to a separatory funnel, washed with saturated aqueous NaCl solution, and dried over $MgSO_4$. Solvent removal yielded a white solid of 164.0 mg (31.2%). Mp 170−171 °C. ^{1}H NMR (acetone-d_6, ppm): δ 9.72 (br, 2H), 7.87 (d, J = 7.70 Hz, 1H), 7.75 (d, J = 7.75 Hz, 2H), 4.32 (s, 2H), 2.06 (s, 3H). ^{13}C NMR (acetone-d_6, ppm): δ 169.6, 165.5, 151.2, 150.1, 140.7, 109.7, 109.0, 43.7, 24.0. MS (EI): 227(M). Anal. Calcd for $C_9H_{10}ClN_3O_2$: C, 47.48; H, 4.43; N, 18.46. Found: C, 47.42; H, 4.37; N, 18.39%.

2-Acetylamido-6-(2-azido-acetylamido)-pyridine (9). A solution of 7.0 mg (0.11 mmol) of NaN_3 and 22.7 mg (0.1 mmol)

of compound **8** in 30 mL of EtOH/H_2O (v/v, 5:1) was reacted at 70 °C for 15 h. The solvent was removed and the crude product was extracted with CH_2Cl_2. Solvent removal yielded a slightly brown solid of 23.0 mg (98.3%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.60 (s, 1H), 8.42 (s, 1H), 7.82 (m, 3H), 4.20 (s, 2H), 2.22 (s, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 168.6, 164.2, 149.6, 148.3, 140.9, 110.3, 109.5, 52.9, 24.7. MS (EI): 234(M). Anal. Calcd for $C_9H_{10}N_6O_2$: C, 46.15; H, 4.30; N, 35.88. Found: C, 46.08; H, 4.24; N, 35.38%.

U-PPV. To a solution of 37.5 mg (0.1 mmol) of compound **6** and 96 mg (0.1 mmol) of compound **3** in 15 mL of DMF, excess fresh EtONa/EtOH was added. The mixture was stirred at room temperature for 24 h. The resulting solution was poured into 50 mL of 1 N HCl aqueous solution, and the product was filtered off. The crude product was redissolved in 2 mL of $CHCl_3$ and poured into 30 mL of methanol 2×. The precipitate was filtered off and dried at room temperature for 6 h to give a yellow powder of 28.5 mg (46.9%). FTIR (KBr pellet, cm^{-1}): 2954, 2867, 1684, 966. ^{1}H NMR ($CDCl_3$, ppm): δ 10.00 (br, 1H), 7.99−8.61 (br, 5H), 6.99−7.70 (br, 5H), 6.74−6.84 (br, 3H), 5.59 (s, 1H), 4.36 (br, 2H), 4.05 (br, 4H), 3.73 (br, 2H), 2.24 (br, 2H), l.83 (br, 4H), l.43 (br, 8H), 0.88 (br, 6H). Anal. Calcd for $(C_{39}H_{43}N_3O_4)_n$: C, 75.82; H, 7.02; N, 6.80. Found: C, 73.21; H, 6.90; N, 6.01%. GPC (THF): Mw 3440, Mn 1750, Mz 5460, PDI l.97.

In the present case, it was difficult to provide spectroscopic arguments on the E:Z stereochemistry of the polymer U-PPV, however it did not have any influence on the supramolecular assembly of DAP-C_{60} with the polymer.

DAP-C60. A solution of 11.7 mg (0.05 mmol) of compound **9** and 36.0 mg (0.05 mmol) of C_{60} in 20 mL of chlorobenzene was refluxed for 12 h under nitrogen, and then cooled to room temperature. The solvent was removed and the product was chromatographed to remove unreacted C_{60} using toluene as elute and to then give the product 14.4 mg (31.1%) using toluene/methanol (5:1) as elute. FTIR (KBr pellet, cm^{-1}): 1684, 527. ^{1}H NMR ($CDCl_3$, ppm): δ 8.61 (br, 2H), 7.96 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 4.21 (s, 2H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 171.86, 168.45, 149.65, 148.24, 146.72, 144.90, 144.72, 144.55, 143.78, 143.39, 143.12, 142.99, 142.85, 142.07, 141.72, 141.49, 141.31, 140.97, 139.90, 110.07, 109.58, 83.22, 54.34, 37.82. MS (MALDI-TOF): 927 (M + 1), 949 (M + Na^+).

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