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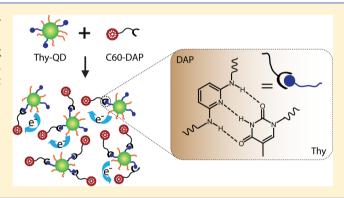


### Engineering the Nanoscale Morphology of a Quantum Dot— Fullerene Assembly via Complementary Hydrogen Bonding Interactions

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Supporting Information

ABSTRACT: We have demonstrated controlled assembly between CdSe quantum dots (QDs) and a fullerene (C60) derivative via complementary three-point hydrogen bonding interactions. The recognition-mediated assembly facilitated an interpenetrated network morphology and hence efficient charge transfer from QD to C60.



ontrolled nanoscale assembly of disparate materials is a powerful tool for producing functional materials with synergistic properties. 1,2 Although top-down lithographic approaches have been used to generate high-resolution multicomponent patterned features, 3,4 high costs and a limited set of suitable materials inhibit their use in commercial applications. Bottom-up approaches through self-assembly provide an alternative route to assembling materials on the molecular scale. 5,6 Self-assembled structures combining building blocks such as colloidal nanoparticles, <sup>7,8</sup> amphiphilic surfactants, <sup>9</sup> and synthetic block copolymers <sup>10,11</sup> have found applications in sensing, <sup>12</sup> bioseparation, <sup>13</sup> catalysis, <sup>14</sup> and ontoelectronics <sup>15</sup> optoelectronics.1

The self-assembly of two or more materials can exhibit diverse morphologies depending upon kinetic and thermodynamic parameters. This behavior imposes stringent preparation requirements if a particular morphology is essential for a specific application. For example, organic (or hybrid) solar cells require an interpenetrating network of donor and acceptor materials at the dimension of their exciton diffusion length (usually 5–10 nm). This "bulk heterojunction" morphology provides an extensive interface between the two materials as well as continuous pathways that facilitate charge separation and transport, respectively.<sup>17</sup> However, in most cases mixing of the donor and acceptor results in macrophase separation. The larger domain size and discontinuous network of the donor and acceptor materials result in charge recombination and ultimately low efficiency of the solar cells.<sup>18</sup>

Here we demonstrate how recognition-mediated assembly based on complementary interactions can give rise to controlled donor-acceptor morphologies. The assembly process was driven by the diamidopyridine-thymine threepoint hydrogen bonding interactions, <sup>19–23</sup> where thyminefunctionalized CdSe quantum dots (Thy-QDs) and diamidopyridine-functionalized fullerene (C60-DAP) were utilized as the donor and acceptor materials, respectively (Scheme 1). Because of the complementary interactions, interpenetrated network of Thy-QD and C60-DAP was generated, facilitating charge transfer from CdSe QD to C60.<sup>24,25</sup> As a control system that cannot participate in hydrogen bonding, N(3)-methyl thymine-functionalized CdSe QDs (MeThy-QDs) were prepared (Scheme 1).

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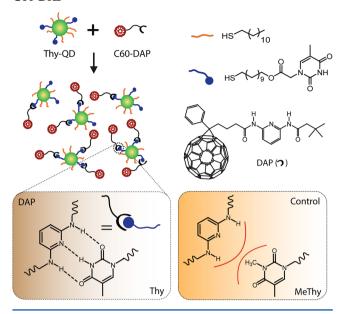
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## Scheme 1. Recognition-Mediated Assembly of Thy-QD and C60-DAP



The addition of C60-DAP to Thy-QDs in noncompetitive solvents such as dichloromethane (DCM) and chloroform resulted in the formation of quantum dot—fullerene (QD—C60) nanocomposite assemblies. Structural characterization of the assembly was done using transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS). The TEM image of pristine Thy-QDs shows monodisperse nanoparticles of 3 nm diameter (Figure 1a). However, clusters of sizes 4 to 6

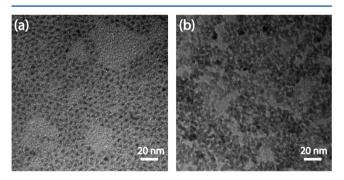
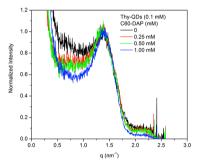


Figure 1. Transmission electron microscopy images of Thy-QDs (a) alone and (b) in the presence of C60-DAP.

nm were observed in the presence of C60-DAP (Figure 1b), indicating that C60-DAP made a shell around each Thy-QD. In contrast to Thy-QDs, no such clusters were observed upon addition of C60-DAP to MeThy-QDs. Instead, the TEM image showed submicrometer-sized aggregates (Figure S1). It has been established that C60 molecules tend to self-aggregate in different solvents. Because there were no complementary hydrogen bonding interactions between MeThy-QD and C60-DAP, the large aggregates suggested macrophase separation of MeThy-QDs and C60-DAP molecules. The control results prove that the complementary nature of the diamidopyridine—thymine interactions was key to the assembly between the Thy-QD and C60-DAP units.

SAXS provides quantitative information about particle organization via plotting the scattering intensity at different wave vectors. The intensity peaks are interpreted as the

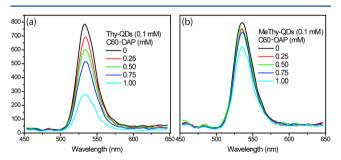
scattering from a collection of particles with a distribution of repeated distances. The average interparticle spacing (d) can be calculated using  $d=2\pi/q$ , where q is a wave vector that corresponds to the maximum scattering intensity. Samples for the SAXS measurements were prepared via drop casting a nanocomposite solution on kapton films. For Thy-QDs, the main peak appeared at 1.40 nm<sup>-1</sup>, corresponding to an interparticle spacing of 4.48 nm. This result is concurrent with 3 nm QDs spaced only by the monolayer of ligands. For QD-C60 clusters, a decrease in the scattering intensity peak width was observed with the increment of C60-DAP (Figure 2). The sharpening of the peak was attributed to the increased



**Figure 2.** Small-angle X-ray scattering profiles of Thy-QDs in the presence of C60-DAP.

organization of QDs due to assembly formation (Scheme 1). The increased organization in the nanocomposite was further supported by the appearance of a second-order shoulder peak observed at 2.25 nm<sup>-1</sup>.

It has been reported that in a CdSe-C60 nanocomposite the quenching of QDs fluorescence is a clear indication of charge transfer from the excited state of CdSe QD to C60 as a result of their favorable band gap offset. Figure 3a shows the steady-



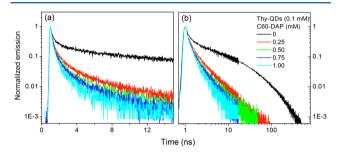
**Figure 3.** Steady-state fluorescence spectra of solutions of (a) Thy-QDs and (b) MeThy-QDs in the presence of C60-DAP at an excitation wavelength of 410 nm.

state fluorescence spectra of solutions of Thy-QDs in the presence of C60-DAP. Because of the heavy overlap of absorption spectra of Thy-QDs and C60-DAP at all wavelengths below 520 nm (Figure S2), the excitation at 410 nm led to the simultaneous excitation of both Thy-QDs and C60-DAP. Emission from Thy-QDs was observed at 540 nm. The emission from the C60 moiety (at 705 nm) was found to be very weak (Figure S5). With increasing concentration of C60-DAP, a decrease in the fluorescence intensity of Thy-QDs was observed, but no significant change in the emission of MeThy-QDs (Figure 3b) reconfirmed that complementary hydrogen bonding was responsible for the Thy-QD and C60-DAP interaction. The results in Figure 3 also demonstrate that the

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interaction between two components in the recognitionmediated assembly can be switched on and off through the choice of recognition elements. The quenching behavior was also observed in the solid state (Figure S6), suggesting that the hydrogen-bonded host—guest complexes were trapped in the thin films.

The interaction between Thy-QD and C60-DAP was further investigated by recording and analyzing the fluorescence decay profiles of Thy-QDs in the presence of C60-DAP (Figure 4).

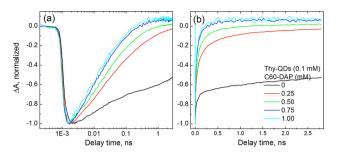


**Figure 4.** Fluorescence decay curves of Thy-QDs in the presence of C60-DAP. The curves in plots a and b differ only in their *x*-axis scales.

The excitation wavelength was chosen as 467 nm. The fluorescence decay of pristine Thy-QDs has nonexponential character. Initial multiexponential decay corresponds to the radiative recombination of neutral and singly and doubly charged excitons.<sup>28</sup> At times longer than ~200 ns, their fluorescence decays according to a power law with a time constant of  $\sim -2.2$  (i.e.,  $1/t^{2.2}$ , Figure 4b). This phenomenon was observed and discussed by us in the previous publication.<sup>22</sup> In the presence of C60-DAP, the fluorescence decays of Thy-QDs remained highly nonexponential (Figure 4). We fitted the decays to a multiexponential function, and the corresponding lifetimes are presented in Table S1. The lifetime of Thy-QDs in the presence of C60-DAP was found to be shorter compared to that of Thy-QDs alone, further supporting the deactivation of the charge-separated state of Thy-ODs via charge transfer from QD to C60. In contrast to the QD lifetimes, no variation in C60 lifetimes was detected through all of the QD-C60 nanocomposite samples (Table S1), and the values were remarkably close to the published value of the C60 fluorescence lifetime in toluene (1.17 ns).<sup>30</sup>

The charge transfer between Thy-QD and C60-DAP was confirmed using subpicosecond transient absorption (TA) measurements. Figure S3 shows the TA spectra of Thy-QDs in the presence of C60-DAP recorded at subpicosecond to nanosecond time intervals after 385 nm laser excitation. The bleaching of the Thy-QD band at 527 nm in the TA spectra represents the charge separation after band gap excitation whereas the bleaching recovery signifies the recombination of the photoinduced charges. The kinetics of Thy-QD ground-state bleaching recovery is shown in Figure 5. In the presence of C60-DAP, the enhanced bleaching recovery of Thy-QDs suggested a secondary deactivation pathway, confirming the charge transfer from QD to C60. Apple 24,25

In conclusion, we have developed a recognition-mediated assembly of CdSe quantum dots and a fullerene derivative via complementary interactions. The introduction of recognition elements capable of complementary three-point hydrogen bonding interactions generated self-assembled interpenetrated structures of CdSe QDs and C60 molecules. As a result, efficient charge transfer from excited CdSe QD to C60 was



**Figure 5.** Bleaching recovery kinetics of Thy-QDs in the presence of C60-DAP at 527 nm after 385 nm laser excitation. The curves in plots a and b differ only in their *x*-axis scales.

observed. We believe that the complementary interactions offer a great opportunity for constructing nanoscale assemblies of polymers and/or small molecules that otherwise aggregate via phase segregation. This recognition-mediated donor—acceptor assembly model could prove very useful in developing bulk heterojunctions for next-generation photovoltaics.

#### ASSOCIATED CONTENT

#### Supporting Information

Synthesis of C60-DAP and CdSe QDs. Thymine-functionalized QDs via ligand exchange. Preparation of the QD-C60 nanocomposite. TEM of a MeThy-QDs and C60-DAP mixture. Fluorescence lifetimes and TA spectra of QD-C60 nanocomposite samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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