

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/236041113>

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

ARTICLE in LANGMUIR · MARCH 2013

Impact Factor: 4.46 · DOI: 10.1021/la4007372 · Source: PubMed

CITATIONS

8

READS

23

9 AUTHORS, INCLUDING:



Vikas Nandwana

Northwestern University

43 PUBLICATIONS 795 CITATIONS

SEE PROFILE



Kyril M Solntsev

Georgia Institute of Technology

87 PUBLICATIONS 2,382 CITATIONS

SEE PROFILE



Gulen Yesilbag Tonga

University of Massachusetts Amherst

28 PUBLICATIONS 251 CITATIONS

SEE PROFILE



Vincent M Rotello

University of Massachusetts Amherst

596 PUBLICATIONS 23,384 CITATIONS

SEE PROFILE

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

Vikas Nandwana,<sup>†</sup> Luis A. Serrano,<sup>‡</sup> Kyril M. Solntsev,<sup>§</sup> Bernd Ebenhoch,<sup>||</sup> Qian Liu,<sup>†,⊥</sup> Gulen Y. Tonga,<sup>†</sup> Ifor D. W. Samuel,<sup>||</sup> Graeme Cooke,<sup>‡</sup> and Vincent M. Rotello<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of Massachusetts Amherst, 710 North Pleasant Street, Amherst, Massachusetts 01003, United States

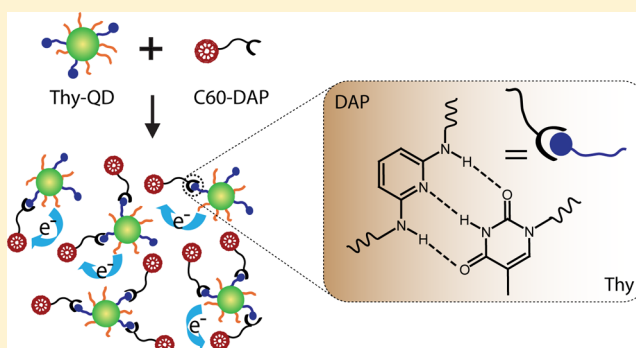
<sup>‡</sup>GCPOC, WestCHEM, School of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

<sup>§</sup>School of Chemistry and Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive, Atlanta, Georgia 30332-0400, United States

<sup>||</sup>Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St. Andrews, North Haugh, St. Andrews KY16 9SS, U.K.

## 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.



Controlled nanoscale assembly of disparate materials is a powerful tool for producing functional materials with synergistic properties.<sup>1,2</sup> Although top-down lithographic approaches have been used to generate high-resolution multicomponent patterned features,<sup>3,4</sup> 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.<sup>5,6</sup> 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 optoelectronics.<sup>15</sup>

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).<sup>16</sup> 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 three-point hydrogen bonding interactions,<sup>19–23</sup> where thymine-functionalized 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).

**Special Issue:** Interfacial Nanoarchitectonics

**Received:** February 27, 2013

**Revised:** March 11, 2013

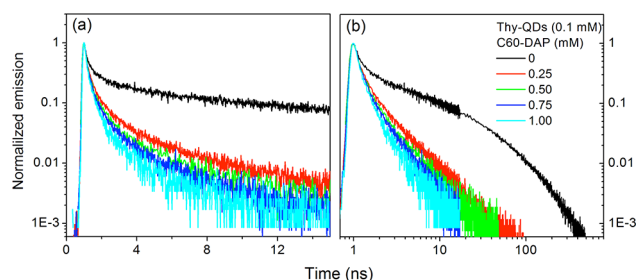
**Published:** March 13, 2013





interaction between two components in the recognition-mediated 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).

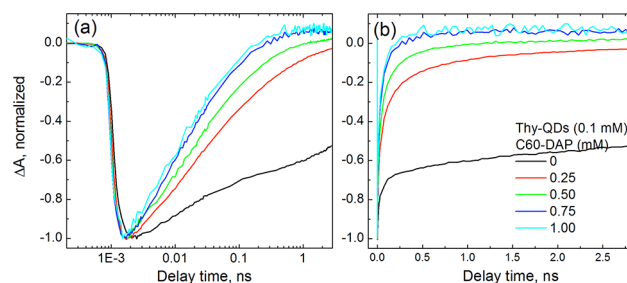


**Figure 4.** Fluorescence decay curves of Thy-QDs in the presence of C60-DAP. The curves in plots a and b differ only in their x-axis scales.

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  $\sim 200$  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>29</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-QDs 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.<sup>24,25</sup> 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.<sup>24,25</sup>

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>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [rotello@chem.umass.edu](mailto:rotello@chem.umass.edu). Fax: +1 413-5452058.

### Present Address

<sup>†</sup>School of Chemistry and Environment, Beihang University, Beijing 100191, China.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This research was supported as part of the Polymer-Based Materials for Harvesting Solar Energy, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under award no. DE-SC0001087, by the National Science Foundation (NSF) under award nos. CHE-1025889 and 1213047, and the EPSRC. Q.L. was supported by the China Scholarship Council for the State Scholarship Fund. We thank Joseph Perry (Georgia Tech) and the members of his group for help with transient absorption measurements.

## ■ REFERENCES

- (1) Brinker, C. J.; Lu, Y.; Sellinger, A.; Fan, H. Evaporation-induced self-assembly: nanostructures made easy. *Adv. Mater.* **1999**, *11*, 579–85.
- (2) Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Thurn-Albrecht, T.; Russell, T. P.; Rotello, V. M. Self-assembly of nanoparticles into structured spherical and network aggregates. *Nature* **2000**, *404*, 746–748.
- (3) Nie, Z.; Kumacheva, E. Patterning surfaces with functional polymers. *Nat. Mater.* **2008**, *7*, 277–290.



- (4) Nandwana, V.; Mout, R.; Yeh, Y.-C.; Dickert, S.; Tuominen, M.; Rotello, V. M. Patterning of protein/quantum dot hybrid bionanostuctures. *J. Inorg. Organomet. Polym.* **2013**, *23*, 227–232.
- (5) Zhang, S. C. Fabrication of novel biomaterials through molecular self-assembly. *Nat. Biotechnol.* **2003**, *21*, 1171–78.
- (6) Nandwana, V.; Subramani, C.; Eymur, S.; Yeh, Y.-C.; Tonga, G. Y.; Tonga, M.; Jeong, Y.; Yang, B.; Barnes, M. D.; Cooke, G.; Rotello, V. M. Recognition-mediated assembly of quantum dot polymer conjugates with controlled morphology. *Int. J. Mol. Sci.* **2011**, *12*, 6357–6366.
- (7) King, S.; Crego-Calama, M.; Reinhoudt, D. N. Self-assembling nanoparticles at surfaces and interfaces. *ChemPhysChem* **2008**, *9*, 20–42.
- (8) Grzelczak, M.; Vermant, M.; Furst, E. M.; Liz-Marzan, L. M. Directed self-assembly of nanoparticles. *ACS Nano* **2010**, *4*, 3591–3605.
- (9) Wang, Y.; Xu, H.; Zhang, X. Tuning the amphiphilicity of building blocks: controlled self-assembly and disassembly for functional supramolecular materials. *Adv. Mater.* **2009**, *21*, 2849–2864.
- (10) Park, C.; Yoon, J.; Thomas, E. L. Enabling nanotechnology with self assembled block copolymer patterns. *Polymer* **2003**, *44*, 6725–6760.
- (11) Krausch, G.; Magerle, R. Nanostructured thin films via self-assembly of block copolymers. *Adv. Mater.* **2002**, *14*, 1579–1583.
- (12) You, C. C.; Miranda, O. R.; Gider, B.; Ghosh, P. S.; Kim, I. B.; Erdogan, B.; Krovi, S. A.; Bunz, U. H.; Rotello, V. M. Detection and identification of proteins using nanoparticle–fluorescent polymer ‘chemical nose’ sensors. *Nat. Nanotechnol.* **2007**, *2*, 318–323.
- (13) Yang, H. H.; Zhang, S. Q.; Chen, X. L.; Zhuang, Z. X.; Xu, J. G.; Wang, X. R. Magnetite-containing spherical silica nanoparticles for biocatalysis and bioseparations. *Anal. Chem.* **2004**, *76*, 1316–1321.
- (14) Wang, C.; Daimon, H.; Lee, Y.; Kim, J.; Sun, S. Synthesis of monodisperse Pt nanocubes and their enhanced catalysis for oxygen reduction. *J. Am. Chem. Soc.* **2007**, *129*, 6974–6975.
- (15) Zhao, Y. S.; Fu, H.; Peng, A.; Ma, Y.; Liao, Q.; Yao, J. Construction and optoelectronic properties of organic one-dimensional nanostructures. *Acc. Chem. Res.* **2010**, *43*, 409–418.
- (16) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.
- (17) Yang, X.; Loos, J. Toward high-performance polymer solar cells: the importance of morphology control. *Macromolecules* **2007**, *40*, 1353–1362.
- (18) Hoppe, H.; Sariciftci, N. S. Morphology of polymer/fullerene bulk heterojunction solar cells. *J. Mater. Chem.* **2006**, *16*, 45–61.
- (19) Beijer, F. H.; Sijbesma, R. P.; Vekemans, J. A. J. M.; Meijer, E. W.; Kooijman, H.; Spek, A. L. Hydrogen-bonded complexes of diaminopyridines and diaminotriazines: opposite effect of acylation on complex stabilities. *J. Org. Chem.* **1996**, *61*, 6371–6380.
- (20) Shi, Z.; Li, Y.; Gong, H.; Liu, M.; Xiao, S.; Liu, H.; Li, H.; Xiao, S.; Zhu, D. Self-assembly and characterization of supramolecular [60]fullerene-containing 2,6-diacylamidopyridine with uracil derivative by hydrogen-bonding interaction. *Org. Lett.* **2002**, *4*, 1179–1182.
- (21) Fang, H. J.; Wang, S.; Xiao, S. Q.; Yang, J. L.; Li, Y. L.; Shi, Z. Q.; Li, H. M.; Liu, H. B.; Xiao, S. X.; Zhu, D. B. Three-point hydrogen bonding assembly between a conjugated PPV and a functionalized fullerene. *Chem. Mater.* **2003**, *15*, 1593–1597.
- (22) Huang, C.-H.; McClenaghan, N. D.; Kuhn, A.; Hofstraat, J. W.; Bassani, D. M. Enhanced photovoltaic response in hydrogen-bonded all-organic devices. *Org. Lett.* **2005**, *7*, 3409–3412.
- (23) Sanchez, L.; Martin, N.; Guldi, D. M. Hydrogen-bonding motifs in fullerene chemistry. *Angew. Chem., Int. Ed.* **2005**, *44*, 5374–5382.
- (24) Bang, J. H.; Kamat, P. V. CdSe quantum dot–fullerene hybrid nanocomposite for solar energy conversion: electron transfer and photoelectrochemistry. *ACS Nano* **2011**, *5*, 9421–9427.
- (25) Shibu, E. S.; Sonoda, A.; Tao, Z. Q.; Feng, Q.; Furube, A.; Masuo, S.; Wang, L.; Tamai, N.; Ishikawa, M.; Biju, V. Photo-fabrication of fullerene-shelled quantum dots supramolecular nanoparticles for solar energy harvesting. *ACS Nano* **2012**, *6*, 1601–1608.
- (26) Sun, Y. P.; Ma, B.; Bunker, C. E.; Liu, B. All-carbon polymers (polyfullerenes) from photochemical reactions of fullerene clusters in room-temperature solvent mixtures. *J. Am. Chem. Soc.* **1995**, *117*, 12705–12711.
- (27) Rudalevige, T.; Francis, A. H.; Zand, R. Spectroscopic studies of fullerene aggregates. *J. Phys. Chem. A* **1998**, *102*, 9797–9802.
- (28) Galland, C.; Ghosh, Y.; Steinbrück, A.; Sykora, M.; Hollingsworth, J. A.; Klimov, V. I.; Htoon, H. Two types of luminescence blinking revealed by spectroelectrochemistry of single quantum dots. *Nature* **2011**, *479*, 203–208.
- (29) Nandwana, V.; Fitzpatrick, B.; Liu, Q.; Solntsev, K. M.; Yu, X.; Tonga, G. Y.; Eymur, S.; Tonga, M.; Cooke, G.; Rotello, V. M. Fluorescence resonance energy transfer in recognition-mediated polymer-quantum dot assemblies. *Polym. Chem.* **2012**, *3*, 3072–3076.
- (30) Kim, D.; Lee, M. Observation of fluorescence emission from solutions of C60 and C70 fullerenes and measurement of their excited-state lifetimes. *J. Am. Chem. Soc.* **1992**, *114*, 4429–4430.