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Thermoreversible Covalent Self-Assembly of Oligo(*p*-phenylenevinylene) Bridged Gold Nanoparticles

Xiaofeng Liu,^{†,§} Huibiao Liu,^{*,†} Weidong Zhou,^{†,§} Haiyan Zheng,^{†,§} Xiaodong Yin,^{†,§} Yuliang Li,^{*,†} Yanbing Guo,^{†,§} Mei Zhu,^{†,§} Canbin Ouyang,^{†,§} Daoben Zhu,[†] and Andong Xia[‡]

[†]Beijing National Laboratory for Molecular Sciences (BNLMS), CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China, [‡]State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China, and [§]Graduate University of Chinese Academy of Sciences, Beijing 100190, P. R. China

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Organic-inorganic hybrids have been fabricated through mild Diels-Alder cross-linking between maleimide bearing oligo(*p*-phenylenevinylene) (OPV) and furan functionalized gold nanoparticles with diameter smaller than 2 nm. The OPV ligands afford strong reaction ability toward furan group due to their maleimide moieties. These small gold nanoparticles form close-packed homogeneous hybrids with well-defined interfaces by incorporating OPV ligands in solutions. Covalent assembly and disassembly of gold nanoparticles can be achieved by repeated thermal stimuli on as-obtained hybrids, which can be monitored by fluorescence changes of OPVs and surface plasmon resonance absorption. Moreover, the dramatic photophysical properties and assembly behavior of these hybrids allow this procedure to be performed as a smart assay for monitoring the process of the Diels-Alder reaction.

1. Introduction

During the past decade, scientists have developed techniques for synthesizing new materials on the nanoscale, especially nanoparticles.¹⁻⁴ Still, the design and synthesis of nanoparticle materials with controlled properties is a significant and ongoing challenge. Understanding the structure–property relationships that relate specifically to nanomaterials could lead to new strategy for producing benign, high-performance nanoscale materials. Metal nanoparticles exhibit intense size- and shape-dependent properties due to the surface plasmon resonance (SPR),⁵ which have attracted considerable recent interest as materials due to their characteristic optical and electronic properties.^{6,7} The assembly of metal nanoparticles into defined macromolecular structures provides potential access to nanocomposites featuring useful chemical and optoelectronic applications.⁸ The internal organization of such composite materials on the nanoscale is crucial for determining the desired properties.⁹ Hybrid nanomaterials consisting of both inorganic nanoparticles and organic counterparts have been exploited extensively due to their unique properties that combining the best properties in both materials into one.¹⁰ Unfortunately, favorable properties are often lost arising from poor dispersion of each component within the hybrid materials.

The Diels–Alder reaction is one of the most important ways in which chemists make new carbon–carbon bonds and which has been extendedly used for the preparation of thermally responsive polymers, dendrimers, and biocompatible materials.¹¹ It has also been found useful as a means to modify self-assembled monolayers (SAMs).¹² Recently, new methodologies have been developed to functionalize monolayer-protected gold cluster (MPC) surfaces using Diels–Alder reaction, facilitating further chemical modifications.¹³ Gates et al.¹⁴ reported that the release of a

^{*}Corresponding authors. E-mail: ylli@iccas.ac.cn (Y.L.), liuhb@iccas.ac. cn (H.L.).

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fluorescent dye from core-shell nanoparticles using retro-Diels-Alder reaction. Gold nanoparticle systems possess reversible behaviors which have been investigated extensively in recent researches;¹⁵ for example, Workentin et al.^{15a} demonstrated the reversible formation of 3D MPC assemblies utilizing the reversible Diels-Alder reaction. On the basis of researches in the past decades, Diels-Alder reaction exhibits reversible behavior on the carbon-carbon bond formation, which has been used widely to build thermoreversible polymeric materials with diverse functionalities.^{11,16} However, there is rare report on the thermoreversibility of gold nanoparticle hybrid composites directed by Diels-Alder reaction.^{12,15}

Considering the facile and thermally reversible formation process, the Diels-Alder reaction is expected to lead to development of new methodologies for fabricating novel organicinorganic hybrid nanomaterials with thermoresponsive behavior. Recently, we have reported a developed chemical approach that fabricating organic-inorganic composites by utilizing mild Diels-Alder reaction.¹⁷ The as-prepared hybrid materials exhibit well-defined interfaces and well dispersity in both inorganic nanoparticles and organic conjugated part. Although the organically shelled MPCs have been explored intensively in recent researches, there have been no reports or practical applications of organic fluorophore-nanoparticles concerning covalent selfassembly and thermoswitchable PL properties. Considering the advantages of both covalently assembly and thermal responsiveness, we aim on fabricating such smart materials capable of modulating both MPCs assembly and optical properties upon thermal stimuli. Herein, we demonstrated that maleimide bearing oligo(p-phenylenevinylene) (OPVs) reacts with furan-modified MPCs (F-Au) to form covalently 3D cross-linked structures (Scheme 1). These materials represent PL reversibility and assembly behavior with thermal responsiveness.

2. Experimental Section

General Information. Chemicals and solvents were reagent grades and all commercially available. Compound **4** was synthesized according to previous report.¹⁸ Solvents were redistilled prior to use. The water used throughout all experiments was purified with a Milli-Q equipment. Detailed synthesis routes for **M2** and **M3** are outlined as shown in Scheme 1. Proton and

carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were carried out on Bruker ARX300 and ARX400 spectrometers using tetramethylsilane (TMS) as internal standard; chemical shifts (δ) are given in ppm relative to TMS. Mass spectra were measured with a Bruker Biflex III MALDI-TOF spectrometer and an APEX II FT-ICRMS spectrometer. UV-vis absorption spectra were obtained from sample solutions on a JASCO V-570 spectrophotometer. Fluorescence spectra were obtained on a JASCO FP-6600 fluorimeter. Quartz cuvettes of 1 cm path length were employed. Transmission electron microscopy (TEM) samples were prepared by applying a droplet of sample solution on carbon-coated copper grids (400 mesh) and evaporated. Images of representative areas were recorded on a JEOL JEM-2011 transmission electron microscope operating at 200 kV. Fluorescence lifetimes were measured by a standard timecorrelated single-photon counting (TCSPC) from Ortac at room temperature using 400 nm laser pulses at 4.7 MHz for excitations of both samples. Fluorescence was detected at 450 nm by using a monochromator (EI-121, Edinburgh Instruments) and fast photomultiplier tube (XP2020). Dynamic light scattering experiments were performed on a nano-ZS zen3600 purchased from Malvern Instruments, Ltd., with 600 nm laser. Data were averaged by three times of measurements for each sample.

Synthesis and Characterization of Diethyl 4-Nitrobenzylphosphonate (1). A mixture of 1-(chloromethyl)-4-nitrobenzene (3.0 g, 17.5 mmol) and triethyl phosphite (3.5 g, 21.1 mmol) was heated at 140 °C for 5 h before being cooled to room temperature. The excess triethyl phosphite was removed in vacuo. The residue was purified by silica gel column (400 mesh, petroleum ether/ethyl acetate = 3:1 as eluent) to give pure 1 as brown oil (4.1 g, 85.9%). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 1.26–1.29 (t, 6H), 4.09–4.11 (q, 4H), 3.16–3.21 (d, 2H), 7.47–7.49 (d, 2H), 8.13–8.15 (d, 2H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 16.3, 39.5, 62.2, 123.8, 131.6, 141.5, 144.9. EI MS (MW = 273.22): *m/z*: 273.08.

Synthesis and Characterization of (*E*)-1,2-Bis(4-nitrophenyl)ethane (2). A clear solution of 1 (570 mg, 2.1 mmol) and 4-nitrobenzaldehyde (315 mg, 2.1 mmol) in dry THF (30 mL) was treated with NaH (151 mg, 6.3 mmol) under a nitrogen atmosphere at 50 °C, followed by stirring for 30 min, after which the reaction was quenched with water carefully. Washed the mixture with saturated aqueous NaCl and dried over MgSO₄ anhydrous. Column chromatography (silica gel, 400 mesh, petroleum ether/ethyl acetate = 6:1 as eluent) afforded pure 2 (235 mg, 41.7%) as a pale yellow solid. ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 7.34 (s, 2H), 7.68–7.71 (d, 4H), 8.26–8.28 (d, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 123.8, 127.4, 129.1, 143.6, 147.3. EI MS (MW = 270.24): *m/z*: 270.03.

Synthesis and Characterization of (E)-4,4'-(Ethene-1,2-diyl)dianiline (3). To a suspension of 2 (150 mg, 0.55 mmol) in mixed solvent of ethanol (10 mL) and ethyl acetate (10 mL) was added concentrated HCl(aq) (5 mL) under stirring at room temperature. Subsequently, SnCl₂·2H₂O (1.25 g, 5.5 mmol) was added, and the

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mixture was heated to 80 °C for 5 h. After cooling to room temperature, the reaction mixture was filtered and the precipitate was discarded. The filtrate was concentrated and washed with saturated aqueous NaCl and dried over MgSO₄ anhydrous. After removal of the solvent, it affords pure **3** (112 mg, 96.0%) as yellow solid. ¹H NMR (CDCl₃, 400 MHz, ppm): $\delta = 6.66-6.67$ (d, 4H), 6.84 (s, 2H), 7.29–7.30 (d, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): $\delta = 114.1$, 122.5, 127.4, 129.6, 147.6. EI MS (MW = 210.27): *m/z*: 210.12.

Synthesis and Characterization of (E)-1,1'-(4,4'-(Ethene-1,2-diyl)bis(4,1-phenylene))bis(1*H*-pyrrole-2,5-dione) (M2). A suspension of 3 (90 mg, 0.43 mmol) and maleic anhydride (126 mg, 1.29 mmol) in chloroform (30 mL) was heated to reflux for 8 h. The resulting dark yellow precipitate was filtered, washed with chloroform, and dried. Subsequently, acetic anhydride (5 mL) and sodium acetate (14 mg, 0.17 mmol) were added. The mixture was heated at 100 C for another 1.5 h. The resulting clear solution was poured into ice water after cooling to room temperature. A precipitate was formed after 10 min, and the mixture was vigorously stirred for an additional hour. The precipitate was filtered and washed with cold distilled water, which was further purified by silica gel column (400 mesh, petroleum ether/ethyl acetate = 5:1 as eluent) to afford pure M2 (120 mg, 75.7%) as a beige solid. ¹H NMR (CDCl₃, 400 MHz, ppm): $\delta = 6.94$ (s, 4H), 6.93-6.95 (d, 2H), 7.14-7.16 (d, 4H), 7.89-7.91 (d, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): $\delta = 124.3, 127.4, 128.1, 129.0,$ 131.9, 135.8, 161.8. EI MS (MW = 370.36): m/z: 370.08. The UV-vis absorption spectrum of M2 is shown in Figure S1.

Synthesis and Characterization of 4,4'-(1E,1'E)-2,2'-(2,5-Dibutoxy-1,4-phenylene)bis(ethene-2,1-diyl)bis(nitrobenzene) (5). A clear solution of 4 (1.2 g, 2.3 mmol) and 4-nitrobenzaldehyde (867 mg, 5.7 mmol) in dry THF (50 mL) was treated with NaH (276 mg, 11.5 mmol) under a nitrogen atmosphere at 50 °C, followed by stirring for 30 min, after which the reaction was quenched with water carefully. The mixture was washed with saturated aqueous NaCl and dried over MgSO₄ anhydrous. Column chromatography (silica gel, 400 mesh, petroleum ether/ ethyl acetate = 6:1 as eluent) afforded pure 5 (680 mg, 57.3%) as dark red solid. ¹H NMR (CDCl₃, 400 MHz, ppm): $\delta = 1.03 - 1.06$ (t, 6H), 1.58-1.62 (m, 4H), 1.86-1.93 (m, 4H), 4.08-4.11 (t, 4H), 7.14 (m, 2H), 7.20-7.24 (m, 2H), 7.61 (m, 2H), 7.63-7.65 (d, 4H), 8.16–8.19 (d, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): $\delta = 14.1$, 19.1, 31.8, 68.8, 114.8, 116.0, 123.8, 125.6, 128.5, 129.0, 143.6, 145.9, 147.1. EI MS (MW = 516.58): m/z: 516.31.

Synthesis and Characterization of 4,4'-(1*E*,1'*E*)-2,2'-(2,5-Dibutoxy-1,4-phenylene)bis(ethene-2,1-diyl)dianiline (6). To a suspension of 5 (517 mg, 1.0 mmol) in mixed solvent of ethanol (15 mL) and ethyl acetate (15 mL) was added concentrated HCl(aq) (7 mL) under stirring at room temperature. Subsequently, SnCl₂·2H₂O (2.27 g, 5.5 mmol) was added, and the mixture was heated to 80 °C for 6 h. After cooling to room temperature, the reaction mixture was filtered and the precipitate was discarded. The filtrate was concentrated and washed with saturated aqueous NaCl and dried over MgSO₄ anhydrous. After removal of the solvent, it affords pure 6 (445 mg, 97.5%) as yellow solid. ¹H NMR (CDCl₃, 400 MHz, ppm): $\delta = 1.00-1.04$ (t, 6H), 1.53-1.60 (m, 4H), 1.80-1.87 (m, 4H), 3.74 (br, 4H), 4.05-4.07(d, 4H), 6.67-6.70 (d, 4H), 6.95 (s, 2H), 7.00-7.08 (d, 4H), 7.34-7.36 (d, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): $\delta =$ 14.3, 19.2, 32.0, 69.1, 114.1, 114.9, 116.3, 122.5, 123.9, 125.8, 129.6, 146.0, 147.6. EI MS (MW = 456.62): *m/z*: 456.21.

Synthesis and Characterization of 1,1'-(4,4'-(1E,1'E)-2,2'-(2,5-Dibutoxy-1,4-phenylene)bis(ethene-2,1-diyl)bis-(4,1-phenylene))bis(1H-pyrrole-2,5-dione) (M3). A suspension of 6 (228 mg, 0.5 mmol) and maleic anhydride (147 mg, 1.5 mmol) in chloroform (30 mL) was heated to reflux for 12 h. The resulting dark yellow precipitate was filtered, washed with chloroform, and dried. Subsequently, acetic anhydride (6 mL) and sodium acetate (16.4 mg, 0.2 mmol) were added. The mixture

was heated at 100 °C for another 2 h. The resulting clear solution was poured into ice water after cooling to room temperature. A precipitate was formed after 10 min, and the mixture was vigorously stirred for an additional hour. The precipitate was filtered and washed with cold distilled water, which was further purified by silica gel column (400 mesh, petroleum ether/ethyl acetate = 4:1 as eluent) to afford pure **M3** (145 mg, 47.1%) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 1.01–1.05 (t, 6H), 1.57–1.60 (m, 4H), 1.85–1.89 (m, 4H), 4.06–4.09 (t, 4H), 6.87 (s, 4H), 7.13 (s, 2H), 7.14–7.17 (d, 2H), 7.34–7.37 (d, 4H), 7.41–7.44 (d, 2H), 7.47–7.51 (d, 4H). ¹³C NMR (CDCl₃, 100 MHz, ppm): δ = 14.0, 18.8, 31.7, 68.7, 114.6, 115.9, 123.6, 124.3, 125.3, 128.1, 128.8, 131.9, 135.8, 145.7, 161.5. MALDI TOF MS (MW = 616.70): *m/z*: 616.40. The UV–vis absorption spectrum of **M3** is shown in Figure S1.

Synthesis and Characterization of Furan Ligand. To a solution of furfuryl alcohol (981 mg, 10 mmol) and 11-mercaptoundecanoic acid (2.18 g, 10 mmol) in dry dichloromethane (85 mL) was added 1-ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride (EDC·HCl, 1.92 g, 10 mmol) and 4-(dimethylamino)pyridine (DMAP, 122 mg, 1 mmol). The flask was purged under a N₂ atmosphere. The mixture was stirred at room temperature overnight. After evaporating off the solvent, the residue was redissolved in a small amount of ethyl acetate (30 mL), washed with water, and dried. After purification through silica gel (400 mesh, petroleum ether/ethyl acetate = 7:1 as eluent), it affords pure furan ligand as yellow oil (1.35 g, 45.2%). ¹H NMR (CDCl₃, 400 MHz, ppm): $\delta = 1.26 - 1.38$ (m, 12H), 1.55-1.66 (m, 4H), 2.30-2.34 (t, 2H), 2.49-2.54 (q, 2H), 5.06 (s, 2H), 6.35–6.36 (d, 1H), 6.39–6.40 (d, 1H), 7.42 (s, 1H) ¹³C NMR (CDCl₃, 100 MHz, ppm): $\delta = 24.6, 25.0, 28.2, 28.9,$ 29.0, 29.3, 29.5, 29.6, 33.3, 34.2, 60.4, 107.6, 110.7, 143.6, 152.1, 173.1. MALDI TOF MS (MW = 298.44): m/z 298.16.

Synthesis and Characterization of Furan-Modified MPCs (F-Au) via Direct Method (Scheme 2). Following a modified Brust-Schiffrin method,¹⁴ to a clear solution of THF (40 mL) containing HAuCl₄ (aqueous solution, 0.1 M \times 1 mL) was added dodecanethiol (MD, 20.2 mg, 0.1 mmol) and furan ligand (29.8 mg, 0.1 mmol) under vigorous stirring at room temperature. After 20 min of reaction, a freshly prepared aqueous solution of NaBH₄ (19.0 mg, 0.5 mmol) was added dropwise with a syringe in 10 min. Subsequently, the mixture was stirred for another 1 h to form a clear brown solution without further change in color. After removal of the solvent under reduced pressure, the residue was redispersed in ethanol. Upon repeated centrifugation and washing with ethanol, the obtained brown powder was dried in vacuo overnight to afford F-Au (28 mg). ¹H NMR (CDCl₃, 400 MHz, ppm): $\delta = 0.88$ (br, 6H), 1.26 (br, 50H), 1.54–1.76 (br, 8H), 2.17 (br, 2H), 2.51 (br, 1H), 2.84 (br, 1H), 5.05 (br, 2H), 6.35 (br, 1H), 6.39 (br, 1H), 7.41 (br, 1H). The F-Au stock solution was prepared by dissolving F-Au (10 mg) in degassed THF (10 mL), which was examined by UV-vis absorption spectrum and TEM observation (Figure S3). The average size of F-Au was determined as 1.8 ± 0.4 nm in diameter.

3. Results and Discussion

The OPVs (M2, M3) were obtained in several steps (Scheme 2). Initially, nitro-substituted OPVs were obtained through several Wittig-Horner reactions. After reduction with SnCl₂, the amino-OPVs undergo cyclocondensation with maleic anhydride to afford M2 and M3 in good yields. UV-vis absorption spectra show typical peaks located at 320 nm for M2 and 340, 395 nm for M3, which mainly ascribe to $\pi - \pi^*$ transitions along the OPV backbones. Furan-modified MPCs (F-Au) were synthesized following a modified Brust-Schiffrin method (Scheme 3).¹⁹

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Scheme 3. Synthesis Procedure for Furan-Modified MPCs (F-Au)



The furan ligand was facile prepared before subjected to one-pot synthesis of small furan-modified MPCs. As determined by TEM, the as-obtained MPC was well-dispersed and $\sim 1.8 \pm 0.4$ nm in diameter (Figure S3 in Supporting Information). The Diels-Alder reaction between OPVs and **F-Au** leads to formation of hybrid networks, while the PL from OPV backbones recovered efficiently along reaction time. It is noted that molar ratio of OPVs and **F-Au** plays a key role in both reaction efficiency and physical properties of the resulting hybrid complexes. By performing a concentration-dependent experiment, we found that molar ratio at 12 exhibits best in PL recovery (Figure S4 in Supporting Information). The investigation of photophysical properties and morphologies was carried out in situ to maintain the intrinsic properties from as-obtained OPV-MPCs using asdetermined molar ratio throughout all experiments. The thermal-driven covalent assembly of M3-Au particles with $d_{Au} = 1.8$ nm was investigated in detail. UV-vis absorption studies in toluene indicate an isolated species featuring sum absorption of M3 (395 nm) and F-Au. TEM on samples cast from toluene confirm the presence of isolated particles. After 12 h of Diels-Alder reaction, however, we found that M3-Au self-assemble into large structures in a reversible manner. Evidence for this comes from the observation of a typical SPR absorption band with a maximum at $\lambda = 530$ nm (Figure 1A). While heating the M3-Au solution at 110 °C, the SP band disappears with a spectral position similar to that found before Diels-Alder reaction. Upon cooling at room temperature for 12 h, the SP band reappears at 530 nm. We ascribe the emergence of SP band at 530 nm to a thermoreversible transition from dispersed to aggregated hybrid complexes. The SP band can be interpreted in terms of the Mie



Figure 1. (A) UV-vis absorption of **M3-Au** ($d_{Au} = 1.8 \pm 0.4$ nm, optical path length 1 cm, [**M3-Au**] = 4.2μ M) in toluene. (B) Timedependent PL enhancement on **M3-Au** (open square, $d_{Au} = 1.8$ nm, [**M3-Au**] = 4.2μ M) and data obtained in mixture of **M3** and **MD-Au** (close square). (C) PL spectra of **M3** (5 × 10⁻⁵ M, black curve), **M3-Au** ([**M3-Au**] = 4.2μ M, red curve), and **M3-Au** after being treated at 110 °C for 2 h (blue curve). All the PL spectra were recorded under 395 nm light illumination.

scattering theory results from transition dipoles coupling while metal particles were restricted at close distance. Our assignment is also supported by PL measurements that reveal progressively PL increase and well reversibility upon thermal treatments. M3 exhibits completely quenched PL, which mainly due to conjugation with maleimide moieties.²⁰ The conjugated C=C bond of maleimide is also known to undergo Diels-Alder reaction with furan.²¹ The resulting succinimide group no longer exhibits a strong quenching effect, and the PL of chromophore is recovered. As shown in Figure 1B, the relative PL intensities $(I - I_0)/I_0$ gradually increased as the time prolonged, while *I* denotes the observed PL intensity of **M3-Au** at various stage of Diels-Alder reaction, and I_0 is the original PL intensity of **M3**. Upon repeated thermal treatments, the PL intensities show well-reversible transition states (Figure 1C). These results indicate that **M3** and **F-Au** were progressively cross-linked to form hybrid superstructures through Diels-Alder reaction.

TEM investigation on different reaction stages provides further insight into the formation of M3-Au superstructures. The MPCs remain dispersed within first 1 h without obvious size and shape changes (Figure 2A). After 12 h of reaction, MPCs cross-link to form large-scale self-assemblies consisting of densely packed M3-Au (Figure 2B, also see Figure S6 in Supporting Information). While zooming in, TEM reveals internal structure that the MPCs remain discrete and hold similar void space (Figure 2C and Figure S7 in Supporting Information). This illustrates ordered self-assembly driven by the bridge effect of peripheral OPV. The rigid backbones with covalently bonding on MPC surfaces prevent them from agglomeration, which enable thermally driven disassembly upon retro-Diels-Alder reaction. The reversibility of Diels-Alder reaction has been explored extensively for fabrication of thermally "remendable" polymeric materials without sacrificing stability and specific functionalities.^{4a,22} In our system, the reversibility of M3-Au was examined by monitoring the PL and superstructures changes over repeated thermal treatments. After Diels-Alder reaction, the PL in M3-Au is recovered efficiently as compared to that of M3 (Figure 1C). However, the M3-Au exhibits quenched PL upon treatment at elevated temperature (110 °C) for 2 h. The thermochromic effect reveals that the PL of these hybrids can be switched "on" and "off" with specific thermal stimulus. In other words, the MPCs may undergo a disassembly process to recover dispersed clusters. Upon thermal treatment at 110 °C after five heating cycles, the MPCs remain well-dispersed with little increase in particle diameter and size distribution (Figure 2D). Dynamic light scattering (DLS) experiments were performed on thermal reversible formation of M3-Au hybrids (Figure S8 in Supporting Information). The results show that MPCs remain dispersed with diameter around 2 nm at initial stage. After sufficient cross-linking, the M3-Au hybrid exhibits large-scale aggregation with average diameter of ca. 600 nm, which is in good accordance with TEM observation. We have performed further measurement on samples after retro-Diels-Alder reaction. DLS size distribution data show dramatic decrease in average diameter (ca. 3 nm) of nanoparticles as compared to highly cross-linked hybrids. However, it shows a little increase in diameter in comparison to initial state, which is mainly due to slight agglomeration of nanoparticles under repeated thermal treatments. Figure 3 shows typical Diels-Alder reaction and retro-Diels-Alder between M3 and F-Au, which leads to order self-assembly of MPCs as well as capability of PL modulation in such hybrid systems. At initiate stage, M3 exhibits weak PL emission due to photoinduced electron transfer (PET)

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Figure 2. TEM images obtained at different time of D-A reaction between M3 and F-Au: (A) 15 min, (B) 12 h, (C) magnification of (B), (D) treated at 110 °C after five heating cycles. Red circle in (C) indicates typical ordered aggregation of M3-Au. Arrows in (D) show partly increase in diameter of MPCs after thermal treatment. Scale bar in (B) represents 50 nm; others are 5 nm.

from OPV backbone to maleimide. After efficient Diels-Alder reaction, MPCs are restricted to form close packed assemblies, and the PL emission enhances upon depression of the PET process. Moreover, the cross-linked superstructures can also decompose to release M3 and F-Au (i.e., thermal reversible formation of OPV-MPCs hybrids). It should be pointed out here that thermal treatment on MPCs at high temperature may cause partly detachment of ligands. The ligand-deficient MPCs tend to form large, insoluble aggregates. During each heating cycle, ligand detachment from gold cluster surfaces is regarded as main obstacle for reversibility of covalent assemblies between OPVs and MPCs. Nevertheless, the forward and backward Diels-Alder reaction has very good reversibility even after 20 cycles.

On the basis of the results obtained in both optical and size distribution observations, we suggest that surface-initiated crosslinking progressively occurs between furan group and pedant maleimide at ambient temperature. The sufficient Diels-Alder reaction reveals immobilization of nanoparticles within polymeric network, which exhibit large-scale self-assembled MPC superstructures. Thermally active OPV-MPCs are capable to selfassemble in a reversible manner. After treated under elevated temperature, retro-Diels-Alder reaction leads to decomposition of each component. Thus, the F-Au gets redispersed, which can undergo forward and backward Diels-Alder reaction repeatedly. Specifically, Diels-Alder reaction between M3 and F-Au was further investigated by time-resolved photoluminescence spectroscopy (Figure 4, see Supporting Information for details). The PL decay curve obtained from initial stage of Diels-Alder reaction exhibits dual exponential fitting model. PL lifetime was obtained as $\tau_1 = 328$ ps and $\tau_2 = 2.72$ ns. It is considered that there are mainly physical blend of M3 and F-Au at very early stage of reaction. Thus, Brownian motion of free F-Au leads to collisions between ligands and MPCs. Obviously, both collision



Figure 3. Representative illustration for the thermal reversible Diels–Alder reaction leading to ordered MPC self-assemblies.

state and free state between M3 and F-Au are almost equally proportional. τ_1 mainly arises from M3 and F-Au in collision state because of PET between them, and τ_2 is from intrinsic OPV backbones of free M3. The proportion is calculated as 46% and 54% for τ_1 and τ_2 , respectively, which prove further evidence on Liu et al.



Figure 4. Time-resolved photoluminescence for M3 and F-Au before and after Diels-Alder cross-linking.

the transient state of M3 and F-Au blend. After sufficient Diels-Alder cross-linking, the M3-Au hybrids exhibit PL decay curve as single-exponential fitting model with PL lifetime of $\tau =$ 1.05 ns. In comparison with τ_1 in the physical blend, the longer lifetime owes to depressed PET from OPV backbone to MPC. Additionally, cross-linked M3-Au no longer shows random collision due to covalent restriction between organic ligands and MPCs. It should be noted that PL decay curve of M3-Au shows an initial increase followed by decay as compared to that of physical mixture. This behavior probably dues to energy transfer from SPR absorption of MPCs to bonded OPV ligand. Furthermore, electron transfer in physical mixture of M3 and F-Au leads to sharp rising processes because of the random collisions effects, which is more close to instrument response function (IRF) curve. However, PL investigations from physical mixture of OPVs and furan-deficient MPCs (dodecanethiolate-modified MPCs, MD-Au, same concentration as F-Au) reveal that no PL recovery occurs (Figure 2A), and the MPCs remain dispersed (data not shown). This suggests that there is no interaction between furandeficient MPCs and OPVs, which provides further evidence for the Diels-Alder reaction between OPVs and F-Au.

It is known that either electron transfer or energy transfer between chromophore and gold cluster is considered to be a major pathway for quenching excited state of chromophore.²³ Interestingly, the

present study on the OPV linked MPCs suggests a dramatic PL enhancement (several hundred times) while performing Diels-Alder reaction. We suppose that the reversibility for modulating OPV PL as well as gold clusters assembly/disassembly mainly arises from thermal reversible Diels-Alder reaction. The reasons can be summarized as follows: First, OPVs show totally quenched PL due to PET from OPV backbone to maleimide. After covalently bonding to furan on the MPC surfaces, the intrinsic PL from OPV recovered due to depression of PET process. Second, the size of as-prepared F-Au is too small to support SP band. Thus, the less spectral overlap with emission of OPVs decrease the excited state energy transfer between OPV and F-Au.²⁴ On the basis of present experiment data, we note that the PET process shows less effect on PL recovery during Diels-Alder reaction. This is mainly because that the quenching efficiency induced by PET is less comparable with that of PL enhancement arising from Diels-Alder adducts, and the electron transfer resulted in feeble PL quenching and can be neglected in such systems herein. Third, rigid OPV structures provide interparticle underprop during the formation of OPV-MPCs superstructure. These enable the intrinsic properties of ligand and nanoparticles to be maintained, which facilitating construction and reversible modulation of such well-defined and large-scale ordered superstructures.

In conclusion, we have fabricated organic—inorganic hybrid materials consisting of conjugated oligomer and gold nanoparticles by performing mild Diels—Alder reaction on both sides of the counterparts. The as-prepared hybrid materials exhibit well dispersity and well-defined interfaces between organic component and inorganic nanoparticles. Furthermore, we have demonstrated that thermal modulation of PL and MPCs assembly/disassembly is possible with smart reversibility over repeated heating cycles. With dramatic PL enhancement and well-defined superstructures resulting from hybrid OPV—MPCs, these environmentally stimuli-responsive hybrid materials can be considered as homogeneous and intelligent materials with a variety of novel technological uses.

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Supporting Information Available: Additional large-scale and detailed TEM images of OPV–MPCs, fluorescence lifetime measurements, DLS size distribution data, and Figures S1–S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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