

Quaternary Supramolecular Nanoparticles as a Photoerasable Luminescent Ink and Photocontrolled Cell-Imaging Agent

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Photoswitchable luminescent supramolecular assemblies based on cyclodextrins have attracted considerable attention owing to their potential applications as smart materials, but most of the assemblies reported to date emit green or blue light with low contrast and high interference. In this study, novel photoluminescent red-luminescent quaternary supramolecular nanoparticles (2) are constructed from a dithienylethene derivative (1), a β -cyclodextrin-functionalized ruthenium complex (Ru-HOP-CD), Pluronic F-127, and cetrimonium bromide. Compared with the binary assembly 1@Ru-HOP-CD, the quaternary nanoparticles exhibit high fluorescence resonance energy transfer efficiency, with Ru-HOP-CD acting as the donor and 1 as the acceptor. Owing to the reversible photoswitched interconversion of the two forms of the dithienylethene component, the fluorescence of the nanoparticles could be switched on/off by irradiation with UV or visible light, both in solution and in the solid state. As a result, the nanoparticles could be used as a photoerasable red-luminescent ink and as a photocontrolled cellimaging agent. These functional nanoparticles can be expected to be useful in the fields of information security and biology.

The construction of stimulus-responsive photoluminescent supramolecular assemblies is attracting increasing attention owing to their potential applications in smart materials, cell bioimaging, security technologies, and so on.^[1] Over the past several decades, cyclodextrins (CDs), a class of cyclic oligo-saccharides with six to eight D-glucopyranose units linked by α -1,4-glucoside bonds, have been widely used as convenient building blocks for constructing functional materials because CDs are water-soluble, nontoxic, and commercially available and they can form host–guest complexes with various molecules.^[2] Recently, several CD-based systems that respond to external stimuli have been reported by our group and others.^[3] For instance, we fabricated a photochemically interconvertible supramolecular nanotube–nanoparticle system by secondary assembly of amphiphilic porphyrins and an azobenzene-bridged

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bis(permethyl- β -CD).^[4] However, there have been only a few reports of systems with luminescence that can be switched on and off by an external stimulus^[5] (e.g., heat, pressure, light, or a chemical species) in such a way that information is invisible under one condition but visible under another condition. To the best of our knowledge, the only example is a CD-based anticounterfeiting material that allows luminescence to be switched on and off by heat.^[6] Compared with visual basic security features used to authenticate products, such as holograms,^[7] watermarks,^[8] and metal threads,^[9] such switchable methods would be harder to counterfeit owing to their unpredictable patterns and nonuniform decoding mechanisms and are a high-throughput and low-cost alternative to traditional anticounterfeiting measures.^[10] Compared with other stimuli, light is clean, noninvasive, sustainable, and readily accessible and can

be applied and removed remotely, thus offering both temporal and spatial resolution.^[11] Therefore, we speculated that using photochromic molecules, such as dithienylethene,^[12] to control the fluorescence of a supramolecular assembly would facilitate the development of anticounterfeiting materials.

Since diarylethenes (DAEs) were first reported by Irie and Mohri in 1988,^[13] they have found numerous applications on account of their good reversibility, excellent thermal stability, high photocyclization conversion ratios, and high photoreaction quantum yields, properties that have permitted these compounds to be successfully used in supramolecular metal-organic frameworks,^[14] optical switches, smart surfaces, functional vesicles, information storage media,^[15] and so on. Irradiation of DAEs with light of alternating wavelengths results in reversible interconversion between the open-ring and closed-ring forms, a transformation that is accompanied by changes in color, spectroscopic properties, and polarizability. Chen et al. used this feature to develop a system for protection of confidential information by loading a Eu³⁺ metal-organic framework (ZJU-88) with a dithienylethene derivative whose luminescence could be switched on and off. However, with most of the previously reported DAE-containing systems, the DAEs must be in an organic phase, owing to their poor water solubility, which limits their wider applications.^[16]

In the current study, we fabricated a photoresponsive supramolecular luminescent ink with near-infrared fluorescence by



using a β -CD-functionalized ruthenium complex (Ru-HOP-CD), a perfluorocyclopentene dithienylethene derivative (1), Pluronic F-127, and cetrimonium bromide, which combined to form

quaternary supramolecular nanoparticles (2) held together by hydrophilic–hydrophobic interactions and noncovalent host– guest interactions (Scheme 1). Our previous research showed



Scheme 1. a) Chemical structures of dithienylethene derivative 1 in its ring-opened and ring-closed forms (OF-1 and CF-1), β -CD-functionalized ruthenium complex Ru-HOP-CD, Pluronic F-127, and cetrimonium bromide; and b) schematic illustration of the formation of reversibly photoswitchable quaternary supramolecular nanoparticles OF-2 and CF-2 and their application as a photoerasable luminescent ink.



that Ru-HOP-CD emits ultrahigh near-infrared fluorescence with excellent fatigue resistance, making it an ideal photosensitizer.^[17] Here, we found that owing to the presence of the dithienylethene unit, complex 1 could undergo reversible photocyclization. Notably, the emission of Ru-HOP-CD overlapped poorly with the absorption of ring-opened 1 (OF-1) but showed good overlap with the absorption of ring-closed 1 (CF-1), implying the possibility of photoswitchable fluorescence resonance energy transfer (FRET) from Ru-HOP-CD to CF-1. We also evaluated the fluorescence quenching efficiency of the nanoparticles and found, to our delight, that the ring-opened and ring-closed forms (OF-2 and CF-2, respectively) exhibited higher fluorescence quenching efficiency than a binary co-assembly derived from 1 and Ru-HOP-CD (designated 1@Ru-HOP-CD). Finally, we explored the utility of the nanoparticles as a photoerasable luminescent ink and as a bioimaging agent.

Ru-HOP-CD was synthesized in satisfactory yield by means of our reported method and was fully characterized.^[17] OF-1 was synthesized as shown in Scheme S1, Supporting Information: treatment of **3** with 1-(adamantan-1-yl)-2-bromoethanone in acetone containing K₂CO₃ produced OF-1 (81% yield), which was fully characterized by ¹H and ¹³C NMR spectroscopy and highresolution mass spectrometry. OF-2 nanoparticles were then synthesized by adding an aqueous solution containing Ru-HOP-CD and cetrimonium bromide to a glass vial coated with a thin-film polymer prepared from OF-1 and Pluronic F-127.

The reversible photocyclization and photochromism of 1 were investigated in water, where 5% DMSO was added to increase its solubility (Figure 1). The UV-vis absorption spectrum of OF-1 showed a maximum at 317 nm. Upon irradiation of OF-1 with UV light (254 nm), this peak gradually decreased in intensity and was blue-shifted by ≈23 nm, and simultaneously a new absorption band centered on 620 nm appeared and increased in intensity. These spectral changes were accompanied by an obvious color change, from colorless to blue, owing to the conversion of OF-1 to CF-1. During the conversion process, three clear isosbestic points (at 351, 417, and 502 nm) were observed in the UV-vis absorption spectrum. To our delight, CF-1 could be completely converted back to OF-1 by irradiation at wavelengths greater than 420 nm and, both OF-1 and CF-1 had no obvious fluorescence emission when excited at 365 nm (Figure S3, Supporting Information). More interestingly, interconversion between the two forms could be repeated at least





Figure 1. Changes in the UV–vis spectra of 1 (1.0×10^{-5} M) in water containing 5% DMSO upon irradiation with UV light (254 nm) and visible light (>420 nm). Inset: absorbance changes at 620 nm over multiple irradiation cycles.

five times without any apparent light fatigue. The conversion ratio for transformation of CF-1 to OF-1 by visible-light irradiation was calculated to be \approx 92% on the basis of ¹H NMR spectral data, whereas OF-1 quantitatively afforded CF-1 upon irradiation with UV light (Figure S4, Supporting Information).

The UV–vis spectrum of Ru-HOP-CD showed an absorption maximum at 476 nm, which was attributed to the metalto-ligand charge-transfer band, and an intense absorption at 220–400 nm, which was attributed to the spin-allowed intraligand transition in water (Figure S5, Supporting Information). Upon excitation at 450 nm, Ru-HOP-CD displayed dazzling red fluorescence (Figure S6, Supporting Information). It is well documented that efficient FRET requires good overlap between the absorption band of the acceptor and the emission band of the donor.^[18] The UV–vis spectrum of OF-1 had only one absorption maximum, at 317 nm, which showed poor overlap with the emission band of Ru-HOP-CD. However, CF-1 had two different absorption maxima, at 366 and 620 nm, and the latter band showed excellent overlap with the emission band of Ru-HOP-CD (Figure 2a). On the basis



Figure 2. a) Normalized absorption spectra showing partial overlap between the fluorescence emission of Ru-HOP-CD and the UV–vis absorption of 1; and b) changes in the fluorescence spectrum of 2 in water ($\lambda_{ex} = 365$ nm) upon irradiation with UV light (254 nm).



of these results, we deduced that supramolecular nanoparticles **2** would exhibit substantial photocontrollable FRET due to interaction of the dithienylethene derivative and the ruthenium complex. We verified the photochromic properties of **2** by UV–vis spectroscopy.

Upon irradiation of 2 with UV light, an absorption peak at 590 nm appeared and gradually increased in intensity. After altering the wavelength of the subsequent irradiation with visible light restored the original spectrum. Notably, this process could be repeated several times without any apparent light fatigue, indicating that OF-1 and CF-1 could be interconverted by irradiation at two different wavelengths even after having been incorporated into nanoparticles 2 (Figures S7 and S8, Supporting Information). In addition, the solution turned deep blue upon irradiation at 254 nm and then returned to its original yellow color upon irradiation with visible light (Figure S9, Supporting Information). Additional convincing proof of photo-responsibility came from the change in fluorescence intensity that was observed when the irradiation wavelength was alternated. When 2 was irradiated at 254 nm for an extended period, the intensity of the fluorescence emission at 612 nm (generated at $\lambda_{ex} = 365$ nm) decreased over time (Figure 2b); on the basis of this experiment, the fluorescence quenching efficiency of 2 was calculated to be 96.6%. For comparison, the fluorescence quenching efficiency of 1@Ru-HOP-CD and 1@Pluric F-127@Ru-HOP-CD was only 46% and 70.6%, respectively (Figures S10 and S11 Supporting Information). When 2 was subsequently irradiated with visible light, the fluorescence of the solution returned to its original level (Figure S12, Supporting Information).

The structure of supramolecular nanoparticles 2 was fully characterized by transmission electron microscopy (**Figure 3**) and dynamic light scattering analysis (Figure S13, Supporting Information). Transmission electron microscopy images of OF-2 showed numerous discrete spherical nanoparticles with an average diameter of 175 nm; and they tended to retain their original micro morphologies even after irradiation at 254 nm for 60 s. Dynamic light scattering analysis revealed that OF-2 and CF-2 had average hydrodynamic diameters of \approx 444.23 and 435.64 nm with a narrow diameter distribution (Figure S13, Supporting Information); these values are larger than the value determined by means of transmission electron microscopy, owing to shrinkage of the nanoparticles during air drying.

The zeta potentials of OF-2 and CF-2 were determined to be 11.43 and 7.00 mV, respectively (Figure S14, Supporting Information); and the positively charged surface of the nanoparticles can be expected to facilitate their entry into cells.^[19] Element mapping analysis of the nanoparticles (Figure S15, Supporting Information) confirmed that they contained Ru, derived from Ru-HOP-CD. Generally speaking, visiblelight irradiation of Ru complexes tends to generate reactive oxygen species,^[20] which suggests that these nanoparticles might have biological applications. To our delight, When our nanoparticles were subjected to electron paramagnetic resonance spectroscopy with TEMPO as a radical-trapping agent, their spectrum was typical of that for TEMPO-¹O₂ adducts, confirming the ability of the nanoparticles to produce reactive oxygen species in solution^[21] (Figure S16, Supporting Information).

Owing to the unique and excellent reversibility of the photocyclization reaction and the photochromic performance of nanoparticles 2, they have great potential utility as an invisible water-soluble ink for information-coding and anticounterfeiting applications. In fact, we found that various patterns could be obtained by spraying a solution of 2 onto filter paper. For example, when the English letters NK (for Nankai University) were written on ordinary filter paper with a solution of OF-2 and then dried in air, they were invisible when the paper was viewed under daylight (Figure S17, Supporting Information). However, when exposed to UV light (365 nm), the letters fluoresced bright red, allowing readout of the previously hidden information. Upon irradiation at 254 nm for a few minutes, the red fluorescence of the letters was completely quenched, and the information was concealed (Figure 4a). Interestingly, the letters could be restored to their original state by irradiation at >420 nm, and the encryptiondecryption process could be repeated several times.

We wondered whether the nanoparticles could also be utilized for photocontrolled luminescent labeling of living cells. To evaluate this possibility, we incubated human lung adenocarcinoma cells (A549 cells) with OF-2 (Figure 4b). After incubation for 24 h, the cells exhibited bright red fluorescence, whereas only weak red fluorescence was observed after UV irradiation at 254 nm, owing to FRET from Ru-HOP-CD to CF-1. Our findings give us reason to believe that the supramolecular nanoparticles reported herein will find a wide variety of applications as anticounterfeiting materials and in biological research.



Figure 3. Transmission electron microscopy images of supramolecular nanoparticles 2 a) before irradiation and b) after irradiation at 254 nm for 60 s.







Figure 4. a) Light-triggered reversible anticounterfeiting behavior of nanoparticles **2** sprayed on filter paper and then irradiated alternately at 254 and >420 nm; and b) confocal fluorescence microscopy images of A549 cells incubated with OF-**2** and CF-**2**.

In summary, we constructed supramolecular nanoparticles from perfluorocyclopentene dithienylethene derivative 1, β -CD-functionalized ruthenium complex Ru-HOP-CD, and two other amphiphilic substances. The resulting nanoparticles exhibited photoresponsive luminescence and could be used as a photoerasable luminescent ink and as a cell-imaging agent. These nanoparticles have several potential advantages over other available stimulus-responsive systems. Owing to the efficient FRET between Ru-HOP-CD and 1 and the ability of 1 to undergo reversible photocyclization, the nanoparticles exhibited strong red fluorescence that could be switched on and off by simply alternating the irradiation wavelength. Therefore, we anticipate that these materials will find applications in the fields of information security and biology.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

anticounterfeiting, cell imaging, cyclodextrin, diarylethene, photoerasable luminescent ink

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- a) J. Zhang, W. Ma, X. P. He, H. Tian, ACS Appl. Mater. Interfaces
 2017, 9, 8498; b) Z. Li, G. Wang, Y. Wang, H. Li, Angew. Chem., Int. Ed. 2018, 57, 2194; c) S. Wang, Z. Xu, T. Wang, T. Xiao, X.-Y. Hu, Y.-Z. Shen, L. Wang, Nat. Commun. 2018, 9, 1737.
- [2] a) C. Yang, Y. Inoue, *Chem. Soc. Rev.* 2014, 43, 4123; b) M. Kryjewski, T. Goslinski, J. Mielcarek, *Coord. Chem. Rev.* 2015, 300, 101; c) Z. Liu, M. Frasconi, J. Lei, Z. J. Brown, Z. Zhu, D. Cao, J. Iehl, G. Liu, A. C. Fahrenbach, Y. Y. Botros, O. K. Farha, J. T. Hupp, C. A. Mirkin, J. Fraser Stoddart, *Nat. Commun.* 2013, 4, 1855; d) M. Nakahata, Y. Takashima, H. Yamaguchi, A. Harada, *Nat. Commun.* 2011, 2, 511.
- [3] a) H. L. Sun, Y. Chen, X. Han, Y. Liu, Angew. Chem., Int. Ed. 2017, 56, 7062; b) L. Stricker, E. C. Fritz, M. Peterlechner, N. L. Doltsinis, B. J. Ravoo, J. Am. Chem. Soc. 2016, 138, 4547.
- [4] H. L. Sun, Y. Chen, J. Zhao, Y. Liu, Angew. Chem., Int. Ed. 2015, 54, 9376.
- [5] a) G. Liu, Y. M. Zhang, L. Zhang, C. Wang, Y. Liu, ACS Appl. Mater. Interfaces 2018, 10, 12135; b) H. Wu, Y. Chen, Y. Liu, Adv. Mater. 2017, 29, 1605271; c) J.-C. Zhang, C. Pan, Y.-F. Zhu, L.-Z. Zhao, H.-W. He, X. Liu, J. Qiu, Adv. Mater. 2018, 30, 1804644; d) Y. Su, Y. Zhang, Z. Wang, W. Gao, P. Jia, D. Zhang, C. Yang, Y. Li, Y. Zhao, Angew. Chem., Int. Ed. 2019, https://doi.org/10.1002/anie.201912102; e) K. Jiang, L. Zhang, J. Lu, C. Xu, C. Cai, H. Lin, Angew. Chem., Int. Ed. 2016, 128, 7347; f) J. Yuan, P. R. Christensen, M. O. Wolf, Chem. Sci. 2019, 10, 10113; g) H. Wu, Y. Chen, X. Dai, P. Li, J. F. Stoddart, Y. Liu, J. Am. Chem. Soc. 2019, 141, 6583; h) Y. Liu, F. Han, F. Li, Y. Zhao, M. Chen, Z. Xu, X. Zheng, H. Hu, J. Yao, T. Guo, W. Lin, Y. Zheng, B. You, P. Liu, Y. Li, L. Qian, Nat. Commun. 2019, 10, 2409.
- [6] Z. Wang, Z. Zhang, L. Tao, N. Shen, B. Hu, L. Gong, J. Li, X. Chen, X. Huang, Angew. Chem., Int. Ed. 2019, 58, 9974.
- [7] a) Z. Lin, L. Huang, Z. T. Xu, X. Li, T. Zentgraf, Y. Wang, Adv. Opt. Mater. 2019, 7, 1900782; b) J. Burch, A. Di Falco, Photonics 2019, 6, 8.
- [8] H. Hu, H. Zhong, C. Chen, Q. Chen, J. Mater. Chem. C 2014, 2, 3695.
- [9] V. Costa, D. de Reyer, M. Betbeder, Stud. Conserv. 2012, 57, 112.
- [10] J. Andréasson, U. Pischel, Chem. Soc. Rev. 2018, 47, 2266.
- [11] a) M. Chen, M. Zhong, J. A. Johnson, Chem. Rev. 2016, 116, 10167;
 b) A. Wilson, G. Gasparini, S. Matile, Chem. Soc. Rev. 2014, 43, 1948; c) Y. Hua, A. H. Flood, J. Am. Chem. Soc. 2010, 132, 12838.
- [12] J. Zhang, H. Tian, Adv. Opt. Mater. 2018, 6, 1701278.
- [13] M. Irie, M. Mohri, J. Org. Chem. 1988, 53, 803.
- [14] J. Park, D. Feng, S. Yuan, H.-C. Zhou, Angew. Chem., Int. Ed. 2015, 54, 430.
- [15] D. Kim, H. Jeong, H. Lee, W.-T. Hwang, J. Wolf, E. Scheer, T. Huhn, H. Jeong, T. Lee, Adv. Mater. 2014, 26, 3968.
- [16] Z. Li, G. Wang, Y. Ye, B. Li, H. Li, B. Chen, Angew. Chem., Int. Ed. 2019, 58, 18025.
- [17] H.-G. Fu, Y. Chen, Q. Yu, Y. Liu, Chem. Commun. 2019, 55, 3148.
- [18] L. Hou, X. Zhang, T. C. Pijper, W. R. Browne, B. L. Feringa, J. Am. Chem. Soc. 2014, 136, 910.
- [19] G.-G. Yang, H. Zhang, D.-Y. Zhang, Q. Cao, J. Yang, L.-N. Ji, Z.-W. Mao, *Biomaterials* **2018**, *185*, 73.
- [20] C. S. Burke, A. Byrne, T. E. Keyes, Angew. Chem., Int. Ed. 2018, 57, 12420.
- [21] N. Cheng, Y. Chen, J. Yu, J.-J. Li, Y. Liu, *Bioconjugate Chem.* **2018**, *29*, 1829.