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Core/Sheath Organic Nanocable Constructed with a Master–Slave Molecular Pair for Optically Switched Memories

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Organic photochromic molecule, which can undergo reversible transformation between two different structural forms upon exposure to light of different wavelengths, is a good example of a photoresponsive bistable molecular system and has been suggested for plenty of potential applications ranging from biomedical research to information technology.^[1-11] The development of switches and memories with photochromic molecules has stimulated intense and highly promising interdisciplinary research efforts. Ideally, a device designer would like to have molecules with efficient photochromic switching; switchable electrical, optical, or magnetic properties between the two photochromic states; and good stability for long-term operation. This requirement of all-round properties is a challenge for synthetic chemists to develop such Holy Grail materials. Even materials with efficient photochromic switching and good electrical or fluorescent properties are rare.^[12,13]

Here, we propose a new approach to solve this problem by distributing the above functions to two optoelectronically coupled molecules. Briefly, a molecule with good photochromic switching properties is used as a "master" molecule. Via optoelectronic coupling, the master molecule will control a "slave" molecule that has no photochromic properties but has good electrical and/or optical properties. The essential optoelectronic coupling is achieved here with a core/sheath nanocable structure, which provides intimate contact between the "master" and the "slave" molecules. Through this design, molecules with more specialized functions can be developed individually, thus meeting the need for developing all-round materials.

Here, we demonstrate the above concept with a core/sheath nanocable constructed with two small molecular materials with

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matched energy levels to enable optoelectronic coupling. The photochromic master molecule used here is a diarylethene derivative, 1-[2-methyl-5-phenyl-3-thienyl]-2-[2-methyl-5-(p-(methyl)phenyl)-3-thienyl]-hexafluorocyclo-pentene (MPT-MMPT-HFCP), which has been widely studied for its excellent photochromic properties.^[1–7,14] Coronene is used as the slave molecule for the following reasons: 1) it has a large aromatic system and is a good holetransporting semiconductor, with electrical properties that have potential tunability upon combined use with MPT-MMPT-HFCP; 2) its photoluminescence (PL) spectrum has extensive overlap with the absorption spectrum of MPT-MMPT-HFCP, which may induce efficient intermolecular energy transfer for the emission modulation: and 3) the π - π interaction between polycyclic aromatic molecules would provide driving force for self-assembling into 1D nanocable.^[15,16] With individual coronene/MPT-MMPT-HFCP core/sheath nanocables, non-volatile memory devices with electrical readout have been fabricated and characterized.

Figure 1 shows that sample 1 has a typical cable nanostructure that is several hundreds of nanometers in diameter and several micrometers in length, where the core consists of an aligned nanofibers of diameters of 50-100 nm. The color of sample 1 can be reversibly switched between green and deep blue by irradiating with light of wavelength 365 and 520 nm, respectively (Figure 2c). To clarify the component of the core and the sheath of the nanocable, sample 1 was rinsed with ethanol. After washing, the color of the sample turned from green to yellow, which is the color of coronene. Photochromism could no longer be observed after ethanol washing. These observations hint that the sheath is likely to be MPT-MMPT-HFCP (the photochromic molecule), while the core is composed of coronene. This supposition is further supported by X-ray diffraction (XRD) spectra (Figure S1, Supporting Information) of sample 1, MPT-MMPT-HFCP, and coronene, which show the coexistence of MPT-MMPT-HFCP and coronene crystalline phases within sample 1.

In our synthesis, tetrahydrofuran (THF) is a good solvent for both coronene and **MPT-MMPT-HFCP**. In contrast, the 3:7 v/v ethanol:water mixture is a poor solvent for them. In preliminary experiments, coronene/THF and **MPT-MMPT-HFCP**/THF solutions were separately injected into the ethanol/water mixtures. While nanocrystals were obtained from the coronene solution, **MPT-MMPT-HFCP** can only form an emulsion. Based on these and the above results, we propose a tentative growth mechanism for the formation of the core/sheath nanostructures (Figure S2, Supporting Information).

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Figure 1. The scanning electron microscopy (SEM) image (a) and transmission electron microscopy (TEM) image (b) of the core/sheath nanowires of sample 1.

Upon injection of the coronene/THF solution into the poor solvent, the limited solubility of coronene and the strong intermolecular π - π interactions provide driving forces for the coronene molecules to aggregate and self-assemble quickly into 1D microstructures.^[15,16] After that, the **MPT–MMPT–HFCP** emulsion is adsorbed onto the surface of the coronene nanofibers, which induces de-emulsification at the same time. As a result, **MPT–MMPT–HFCP** molecules gradually crystallize on the surface of the nanofiber and form the core/sheath structure, as shown in Figure S2d (Supporting Information).

The **MPT–MMPT–HFCP** molecule can undergo photochromic reactions between the open-ring and closed-ring isomers by irradiation with UV (365 nm) and visible light (520 nm), respectively (Figure 2b). In the dark, the deep blue color remains stable at room temperature. The absorption spectra of the closed **MPT–MMPT–HFCP** are characterized by the peak at 590 nm, which is assigned to the S₀–S₁ transitions of its closed diarylethene unit.^[1,17] (Figure S3a, Supporting Information). Upon irradiation with 365 nm light, the absorption



Figure 2. The coronene (a) and the photochromism of MPT-MMPT-HFCP (b) and the sample 1 deposited on a 1×1 cm² glass substrate observed by irradiation with light of 365 and 520 nm, respectively (c).



over the 590 nm region by the closed-ring isomer increases with the irradiation dose. Such a change is similar to that observed in other diarylethene derivatives and can be attributed to the cyclization isomerization of the dithienylethene chromophore in **MPT– MMPT–HFCP**.^[18–24] Irradiating the closed isomer with light of 520 nm restores the original spectrum (Figure S3b, Supporting Information), which indicates that the photoinduced cyclization is reversible. The kinetics studies of **MPT–MMPT–HFCP** and sample 1 show they have similar rate constants during the isomerization process (see Supporting Information).

PL of the photochromic compounds has been utilized as a readout signal in memory applications. Unfortunately, many photochromic compounds, including

Unfortunately, many photochromic compounds, including MPT-MMPT-HFCP (Figure S4b, Supporting Information) do not have strong PL emission. For obtaining PL signals, the most commonly used approach is to attach fluorophores covalently to the organic photochromic species.^[25-33] However, it is a difficult task to design and synthesize these multifunctional fluorescent photochromic molecules. Moreover, the tunability of the active absorption bands corresponding to the writing, erasing, and reading processes should be carefully considered such that the reading process will not disturb the memory state. Here, we distribute the "switching" and the "functional" (i.e., the electrical and fluorescent properties) capacities into a pair of master and slave materials. This new approach is demonstrated by application of the coronene/MPT-MMPT-HFCP core/sheath nanocables as non-volatile memory devices. In such devices, the photochromic MPT-MMPT-HFCP molecule is used as the master material to provide the "switching" capacity. The nonphotochromic coronene molecule will be used as the slave

molecule to provide fluorescence and electrical conductivities.

Figure 3a show PL of the core/sheath nanocables after exposure to alternating cycles of UV (365 nm) and visible (520 nm) illumination. Since the PL spectra is the same as that of pure coronene and MPT-MMPT-HFCP has no apparent photoluminescence (Figure S4, Supporting Information), we can reasonably conclude that PL of the core/sheath nanocables is inherited from the coronene slave molecule. As shown in Figure 3, the PL of the core/sheath cables can be reversibly switched between the high intensity ("ON") and the low intensity ("OFF") states upon exposure to visible and UV light, respectively, corresponding to the photochemical conversion between the two states of the MPT-MMPT-HFCP master. Upon exposing to the 365 nm light, the PL intensity gradually decreased within 420 s and then increased in the next 420 s under irradiation with 520 nm light, reversibly (Figure 3b). It can also be seen that upon irradiation with light of 365 or 520 nm,

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Figure 3. The photoluminescence of sample 1 modulated with UV (365 nm) and visible light (520 nm) (a) and the reversibility of the emission at 500 nm of the sample 1 tuned by alternating cycles of UV (365 nm, red area) and visible light (520 nm, blue area) (b).

most of the changes in PL intensity (respectively 85% and 50% of the total changes) occurs over the initial 60 s. The ON/OFF ratio for the PL intensity at 500 nm is as high as \approx 4.5. No sign of fatigue was observed after several cycles. These results show that by switching the state of the master, the fluorescence of the slave can be turned on and off.

This master–slave action poses a question here on the mechanisms by which the master can control the slave. In fact, it can be seen that PL of coronene slave (Figure S4a, Supporting Information), overlaps considerably with the absorption of **MPT–MMPT–HFCP** master (Figure S3a, Supporting Information) over the region between 450 and 600 nm. This hints that the strong photoswitching of the composite nanocables might be induced by an efficient intermolecular energy transfer process.^[34–36] Detail mechanisms of the master–slave action will be discussed later.

For practical applications, non-destructive writing, erasing, and reading processes are required; therefore each process should be independently carried out by irradiating in different regions of the spectrum. In the nanocables, the excitation of coronene incidentally overlaps with the absorption of **MPT–MMPT–HFCP** for the open isomer transforming to the closed isomer. Consequently, the reading process might trigger photoisomerization of the **MPT–MMPT–HFCP** sheath leading to signal destruction. Obviously, such an optical readout process might not be ideal for practical usage. One possible solution is to utilize electrical properties for reading the molecule state. To the best of our knowledge, electrical studies on photochromic molecule are still in their infancy.^[37–42] In particular, the attempt to fabricate a rewritable non-volatile memory device by combining the optical and the electrical properties of a photochromic molecule has not been reported before.

Interestingly, when examining the influence of the photoisomerization of the photochromic sheath on the electrical properties of the semiconducting core, we found that electrical signal could be used as non-destructible readout in our memory devices. Figure 4a shows the typical current densityvoltage (I-V) curves obtained when exposing the nanocables to light with a wavelength of 365 or 520 nm (a schematic of the device can be found in Figure 5). As shown in Figure 4b, the photoconductivity of the nanocable was first demonstrated at the beginning 25 min of the phototunable electrical property measurement. All data in Figure 4b were measured under a bias voltage of 2 V. When irradiated with 520 nm light, the photocurrent of the cable doubled almost instantly (see first and second columns of Figure 4b) with respect to the dark current. The current dropped rapidly back to the dark current after cutting the irradiation (third column of Figure 4b). In our system the switchable component is a diarylethene, which has been shown in previous studies to have poor PL and no photoconductivity; on the contrary, coronene has shown the above properties.^[43] On the other hand, the closed form of diarylethene has more



Figure 4. The *I*–V curves measured upon exposure to 365 and 520 nm light (a). The current measured at the first 25 min and the reversibility of erasing, writing, and reading processes of sample 1 memory device measured under 2 V bias voltage (b); the red area was measured in the dark, the yellow-green area was measured by exposure to 520 nm light, and the blue area was measured by exposed to 365 nm light.

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(b) (c)

Figure 5. A schematic of the device configuration for the memory measurement (a), the prefabricated blank electrode (b), and the nanowires of sample 1 dispersed on the electrode (c).

extended π -conjugated system and high conductivity compared to the open form.^[38,40] If the electrical measurement is really due to the poorly conducting diarylethene, the current should increase upon UV exposure (i.e., opposite of what is observed in the present results). In short, switching of the diarylethene cannot explain the optical read-out as it has no PL properties; it cannot explain the electrical read-out as it will lead to opposite changes in current.

As a memory device, the writing operation was performed by photoirradiating the cable with 365 nm light (the fourth column; blue area in Figure 4b). The reading operation was carried out by turning off the photoexcitation and measuring the current of the device (the third and fifth columns; red area in Figure 4b). The erasing procedure involved the irradiation of the cable with 520 nm (the sixth column). In the writing process, the photocurrent decreases almost by one order of magnitude gradually within 17 min, with a value changing from 3 pA to 0.3 pA that could be recognized as signal "1" in the later reading process. In the erasing procedure, the synergism of the photomodulation of the MPT-MMPT-HFCP master and photoconductivity of the coronene slave induces a nearly 20 times increase on the current, which then reduces to one order in the reading process and can be regard as signal "0". The reversibility of switching between the "1" and "0" states of the device based on the nanocable was also demonstrated in Figure 4b. The two stable states can be reproducibly switched by repeating the writing, reading, and erasing processes with little sign of fatigue after three cycles. In fact, diarylethene derivatives have shown high durability; the isomerization between the open ring and closed ring can be repeated more than 10⁴ times while maintaining satisfactory photochromic qualities.^[1-7,14] Therefore, it is expected that the memory device based on the nanocable would have a reasonable durability. The retention ability of the "1" and "0" states of the device was tested under ambient atmosphere. As found in Figure 6, the devices can preserve the two states for hundreds seconds without any significant degradation. Comparing to some other systems, the finally switching time of the device is longer. As shown in Figure 4b, the switching from "1" and "0" states or from "0" and "1" states are both about 20 min.



Figure 6. Retention characteristic of the sample 1 memory device measured under 2 V bias voltage. Red and black curves show current versus time after the device was switched to "1" and "0" states, respectively.

On the other hand, while we have successfully shown the possibility of electrical read out using the present system, it is noted that the electrical performance is still below those reported by Kronemijer et al. and Whalley et al.^[40,44] For practical highperformance applications, performance enhancement is still needed for the present device. However, the main purpose of this work is to present the new approach of using the master– slave system and the memory device is only used as an example for proofing the concept.

While the exact working mechanisms of our device are not been fully understood, we propose a possible interpretation based on the literature and our theoretical calculation.^[37-42] It is well known that the transport of charge carriers in a semiconductor is easily influenced by traps. For the trapping of holes (the core of the cable, coronene, is a hole-transporting material), there are two cases: 1) the creation of chemical traps: a host material combined with a guest material whose ionization energy is lower (i.e., highest occupied molecular orbital (HOMO) level is higher) than that of the host material and 2) the creation of dipolar traps: the energy of electrostatic interactions between a charge carrier and its surrounding is locally modified by the presence of polar species. The energy states of coronene and open- and closed-MPT-MMPT-HFCP were obtained by theoretical calculation and illustrated in Figure S5 (Supporting Information). The HOMO of the open-MPT-MMPT-HFCP (-6.0 V) is slightly lower than that of coronene (-5.8 V), therefore this open isomer cannot efficiently trap the positive carrier in coronene. However, after transformation to the closed isomer, the HOMO of MPT-MMPT-HFCP is raised to -5.4 V, which is higher than that of coronene. Thus, the closed form of MPT-MMPT-HFCP can act as a trap to the hole carriers of the coronene core. On the other hand, the molecular dipole moment calculations reveal that the dipole moment of MPT-MMPT-HFCP increases from 5.1 D to 5.9 D after isomerizating from the open isomer to closed isomer. The local augment of the dipole moment of the photochromic sheath after UV irradiation means the dipolar traps may also be created for the hole trapping.





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To summarize, we propose a new approach of distributing the photochromic "switching" and the "functional" capacities required for a photochromically controlled device into a master and slave system. Via this approach, photochromic and functional properties can be individually optimized. The concept is illustrated by fabrication and characterization of nonvolatile memory devices with a coronene/**MPT-MMPT-HFCP** core/sheath nanocable, where by switching the photochromic master sheath, the electrical conductance and fluorescence of the semiconducting slave core material can be reversibly tuned. The present approach opens another dimension for the design of photochromic memory devices. By decoupling the switching and the functional properties, the performance of photochromic devices can be easily improved by independently optimizing the master and the slave molecules.

Supporting Information

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

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