The non-covalent assembly of benzene-bridged metallosalphen dimers: photoconductive tapes with large carrier mobility and spatially distinctive conduction anisotropy†

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A newly synthesized benzene-bridged metallosalphen dimer tailored with aliphatic chains is demonstrated for the solution-processed assembly of a π-electronic tape, which shows a large intrinsic carrier mobility, is spatially anisotropic in conduction, forms p- or n-type semiconductors tunable upon doping, is photoconductive and is capable of repetitive switching with large on–off ratios.

In photoconduction, photogenerated charge carriers move towards electrodes and produce an electric current.[1] Studies on such photoresponsive molecules have been an important part of progress in the field of solar energy conversion.[2] Single crystals of certain π-conjugated molecules, *e.g.*, arenes, have been reported to become photoconductive as a result of exciton migration and charge separation at the molecule–electrode interface.[3] However, small arenes absorb photons only in the ultraviolet region, while large arenes with absorption bands extending to the visible region require complicated synthesis, tedious purification and are difficult to process. Moreover, the undesirable photoinduced dimerization and bleaching of arenes deter their application in optoelectronics.[4] During a study on the assembly of conjugated multinuclear metallocomplexes, we serendipitously discovered that these π-electronic metalloconjugates are photoresponsive, robust against irradiation and may avoid the above drawbacks.

Herein, we report a photoconductive tape assembly from a benzene-bridged dinuclear metallosalphen (Chart 1; **1**) *via* a simple solution process (see the ESI†). The tape of **1** absorbs a wide range of visible photon wavelengths efficiently, exhibits an extremely high intrinsic carrier mobility and forms paths for charge carrier transportations with a distinctive spatial anisotropy. It also affords p- or n-type semiconductors that are tunable upon oxidation or reduction. We emphasize that the tape is highly responsive to visible light irradiation, triggers prominent photocurrent generation, shows on–off ratios as high as 9.0 × 10^4 and is capable of repeated on–off switching without deterioration. The molecular design of bridged dinuclear metallocomplexes has led to findings of unusual physical properties and utilities such as catalysts,[5a] the mimicry of biological enzymes,[5b] molecular magnets,[5c] building blocks for coordination polymers[5d] and MOFs.[5e] However, photo functions have remained unexplored to date.[6]

1 exhibits absorption bands at 457, 489 and 522 nm (Fig. 1(a), red curve), which is 122 nm red-shifted from mononuclear reference **2** (Fig. 1(a), black curve). In addition, **1** shows a significantly enhanced molar absorption coefficient ($\varepsilon_{457\text{ nm}} = 7.53 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1}$) that is about 2.6 times as large as that of mononuclear **2** ($\varepsilon_{400\text{ nm}} = 2.87 \times 10^4\ \text{M}^{-1}\ \text{cm}^{-1}$). These results clearly suggest that the π-conjugation is extended over the molecular skeleton, including the salphen subunits. Cyclic voltammetry of **1** in THF (0.5 mM) shows two quasi-reversible redox pairs at −0.48/−0.26 and 0.39/0.67 V *vs.* Ag/AgCl (Fig. 1(b)), indicating that **1** can be both reduced and oxidized at relatively low potentials.[6] In contrast to **1**, **2** displays only oxidation potentials (0.25/0.45 V; Fig. S2, ESI†), while no reduction signals are observed. Calculation at the spin-unrestricted B3LYP/6-31G(d,p) level with the Gaussian 03 package (see the ESI†) revealed that **1** has HOMO–LUMO gaps of 2.6 and 2.8 eV for its α-(spin up) and β-(spin down) electrons, respectively, while **2** has the same α- and β-HOMO–LUMO, with gaps as high as 3.4 eV (Fig. 1(c); Fig. S3, ESI†).

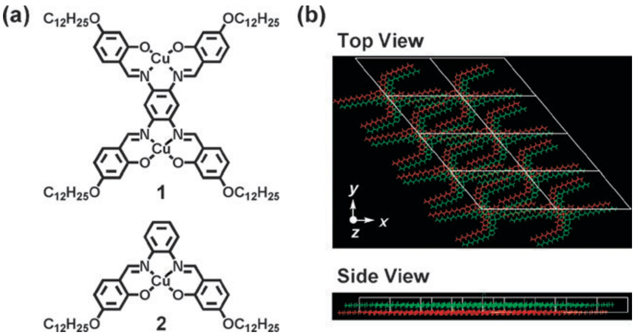

Chart 1 (a) Schematic representations of benzene-bridged copper salphen metallodimer **1** and its mononuclear control **2**. (b) The possible molecular alignment in the tape: top and side views. Molecules of **1** in green are in the same layer and overlap the molecule layer in red. x, y and z are the width, length and thickness directions of the tape, respectively.

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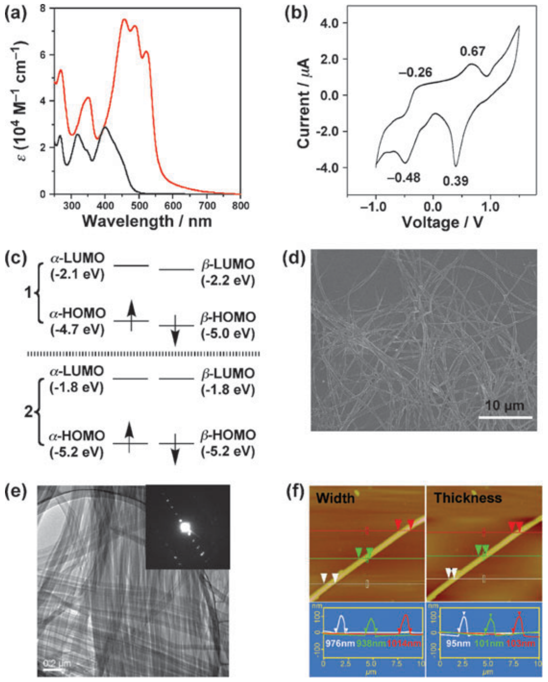

Fig. 1 (a) Electronic absorption spectra of **1** (red curve) and **2** (black curve) in CH_2Cl_2 at 25 °C (9.0×10^{-6} M; at this concentration, no aggregation was observed). (b) CV profile of **1** in THF. (c) HOMO and LUMO levels of **1** and **2**. (d) FE-SEM image. (e) HR-TEM image (inset: SAED image of a single tape). (f) AFM image (10 × 10 μm).

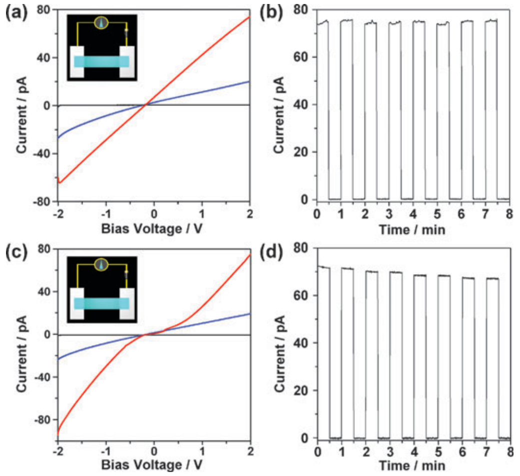

Fig. 2 (a) The *I*–*V* profile of the tapes between a 10 μm-wide Pt gap (black curve, without tapes; blue curve, with tapes; red curve, with iodine-doped tapes). (b) The electric current when a 2 V bias voltage is turned on or off. (c) The *I*–*V* profile of the tapes between a 10 μm-wide Pt gap (black curve, without tapes; blue curve, with tapes; red curve, with hydrazine-doped tapes). (d) The electric current when a 2 V bias voltage is turned on or off.

2 is highly soluble and scarcely aggregates in THF. In contrast, **1** assembles in THF (1.0 mg ml^{-1}) to form tape-shaped aggregates in 83% yield by a heating-and-cooling process. FE-SEM images reveal that the 1D tapes have lengths reaching hundreds of micrometers (Fig. 1(d)). HR-TEM shows that the width of an elementary tape is about 100 nm (Fig. 1(e), inset: the SAED pattern shows the crystalline molecular order). The thickness ranges from 10 to 100 nm (estimated from AFM images; Fig. 1(f)). No other shapes, such as spheres, sheets or 3D objects, were observed. Powder X-Ray diffraction (PXRD) measurements show sharp diffractions at $2\theta = 3.83, 5.07, 6.46, 10.28, 15.73, 20.61$ and $25.71°$ (Fig. S4, blue curve; ESI†). Simulation with molecular modelling and Pawley refinement using Reflex implemented in the Materials Studio[7] package reveals that the monoclinic unit cell of $a = 34.76$, $b = 22.96$ and $c = 6.92$ Å with $\alpha = \beta = 90$ and $\gamma = 130°$ gives a PXRD pattern that mostly fits the experimental observations (Fig. S4b, red curve; ESI†). Accordingly, **1** is most likely to be interlocked *via* aliphatic chain interdigitation to form molecular tapes, and π–π stacking leads to the growth in the thickness direction (Chart 1(b)). Indeed, FT-IR spectroscopy displays CH_2 stretching vibrations at 2849 (ν_{sym}) and 2919 (ν_{asym}) cm^{-1} (Fig. S5, ESI†), demonstrating that the aliphatic chains adopt a stretched conformation and are in a crystalline state. Time-dependent absorption spectroscopy shows a spectral change typical of J-aggregation (Fig. S6, ESI†).[8]

The highly ordered structure of π-conjugated **1** in the tape suggests a high probability of it being electronically semiconducting. We investigated this possibility by measuring its electrical conductivity using a two-probe method with a 10 μm-wide Pt gap. The tape shows an almost linear *I*–*V* profile (Fig. 2(a), blue curve), while the gap itself is silent (black curve). Upon oxidization with iodine, the electrical conductivity increases (Fig. 2(a), red curve), characteristic of a p-type semiconductor. The conductivity can be switched many times without deterioration (Fig. 2(b)). Out of interest, exposure to hydrazine vapor increased the electric current, suggesting an n-type semiconductor character (Fig. 2(c), red curve).[9] The electric current can be on–off switched repeatedly (Fig. 2(d)).

Along these lines, we further investigated the photoconductivity of the tape under visible light irradiation. Since the molecular orientations parallel and perpendicular to the long axis of the tape are different, we utilized two types of electrodes, having different configurations to show the effect of molecular alignment on photocurrent generation. The tapes laid on the Pt gap electrodes show a response to visible light irradiation (> 400 nm), with an increase in electric current (Fig. 3(a), red curve). The photocurrent can be on–off-switched at negative (Fig. 3(b), red curve) and positive (Fig. 3(b), blue curve) bias voltages, with on–off ratios of about 1.6×10^2 and 1.9×10^2, respectively. In contrast, tapes sandwiched between Al/Au electrodes under otherwise identical conditions show a more substantial photocurrent generation (Fig. 3(c)). In this case, the on–off ratio is as large as 9.0×10^4 (Fig. 3(d)),[10] which is 50 times larger than that on Pt gap electrodes. The significant difference in photocurrent generation between the two configurations shows that the molecular alignment has an effect on the conduction. **1** stacks perpendicular to the xy plane of the tape at a π–π distance of about 3.46 Å, while in the *xy* plane, **1** is separated by much larger center-to-center spacings (3.48 and 2.30 nm). Thus, the conduction path perpendicular to the xy plane of the tape is most likely to be superior to the parallel one, leading to a spatially distinctive conduction anisotropy.

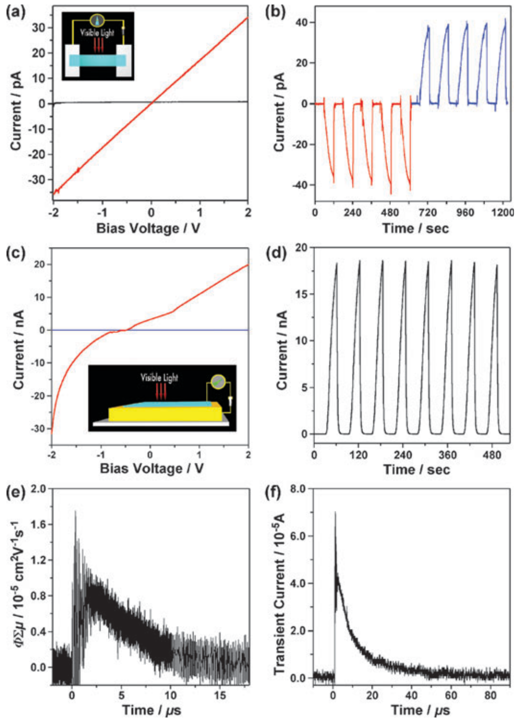

Fig. 3 (a) The *I–V* profiles of the tapes between a 10 μm-wide Pt gap (black curve, without tapes; red curve, with tapes upon visible light irradiation). (b) The photocurrent when the light is turned on or off at −2 V (red curve) and 2 V (blue curve) bias voltages. (c) The *I–V* profiles of tapes sandwiched between Al/Au electrodes (blue curve, without light irradiation; red curve, upon visible light irradiation). (d) The photocurrent when the light is turned on or off at a 2 V bias voltage. (e) The FP-TRMC profile of tapes in Ar at 25 °C upon irradiation with a 355 nm pulse laser at the power of 2.0×10^{16} photons cm^{-2}. (f) The time-of-flight transient conductivity of tapes at a 2 V bias voltage.

We utilized the laser flash photolysis time-resolved microwave conductivity (FP-TRMC) technique to investigate the intrinsic carrier mobility of the tapes.[11] The transient conductivity rises rapidly upon laser irradiation at 355 nm, giving a $\Phi\Sigma\mu$ value of 1.2×10^{-5} cm^2 V^{-1} s^{-1} in Ar gas at the photon density of 2.0×10^{16} photons cm^{-2} (Fig. 3(e)). Since SF_6 gas serves as an electron quencher, in this case, only holes contribute to the conductivity. The tape in SF_6 gas under otherwise identical conditions exhibits a transient conductivity profile similar to that in Ar, giving a $\Phi\Sigma\mu$ value of 1.16×10^{-5} cm^2 V^{-1} s^{-1}. The negligibly small difference in $\Phi\Sigma\mu$ values between Ar and SF_6 gases suggests that holes play a major role in the conduction of the tape itself in the absence of any chemical dopants. In order to determine the number of charge carriers, time-of-flight transient integration was measured at different bias voltages (Fig. 3(f)). The number of charge carriers at 2 V was 3.4×10^{12} and the charge carrier generation yield (Φ = number of charge carriers per photon) was evaluated to be 1.7×10^{-4}. Thus, the minimum carrier mobility ($\Sigma\mu$) was calculated to be 0.068 cm^2 V^{-1} s^{-1}, which is comparable with or higher than those of large arenes, such as assemblies of hexabenzocoronene[12a] and sumanene,[12b] conjugated polymers,[10] and liquid crystalline systems.[12c]

In summary, we have demonstrated a newly synthesized benzene-bridged metallosalphen dimer that can be used to form high quality sub-millimeter-length tapes with large aspect ratios by a high throughput solution process. The π–π interactions, together with van der Waals forces, result in a unidirectional molecular order in the tapes, favoring the formation of carrier paths with a significant anisotropic character. The tapes are capable of harvesting visible light and trigger photocurrent generation with a large on–off ratio. Moreover, their redox nature enables the formation of either p- or n-channel semiconductors. These unique functions, together with their large carrier mobility feature, suggest the great potential of π-conjugated metallocomplexes in developing photofunctional materials and molecular optoelectronics.

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