

|Very Important Paper|

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Organic Two-Dimensional Assembly with Rectification Property Mediated by Cucurbit[8]uril

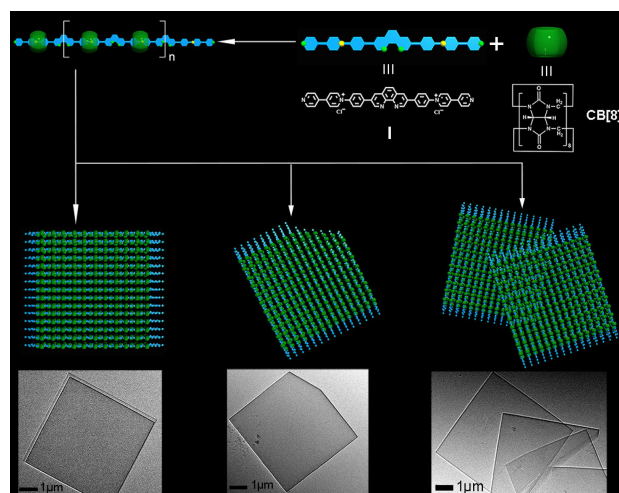
Zhi-Yuan Zhang,^[a] Yong Chen,^{*,[a]} Ji-Wei Qi,^[a] and Yu Liu^{*,[a, b]}

Abstract: We report a highly regular organic two-dimensional assembly made of cucurbit[8]uril and aromatic units that shows peculiar optoelectronic properties. We found that this individual self-assembled microplate displayed a good conductivity under forward bias but nearly no current was detected under reverse bias along the stacking direction. This unique phenomenon is due to the coordination assembly of cucurbit[8]uril with aromatic units and aromatic stacking between layers. Moreover, the fluorescent properties are maintained in the solid state. Our result might show advantages in fabricating optoelectronic devices and help others to design organic two-dimensional materials with specific functions. ■ ■ Please add an email address for Yong Chen ■ ■

Two-dimensional (2D) materials have attracted tremendous attention due to their various applications in optoelectronics, catalysis, biomedicine and so on.^[1] Organic 2D (O2D) materials have the properties of flexibility and light-weight, but the tedious approaches in structural modification and rigorous conditions in construction remain obstacles for their developments and applications.^[2] Supramolecular self-assembly is a good solution due to numerous building blocks,^[3] precise structural control,^[4] and various fabricating methods.^[5] Several successful attempts in constructing supramolecular O2D have been made, such as photoresponsive microplates formed by organic-inorganic hybrid co-assembly,^[6] smart organic two-dimensional materials autonomously formed by mono-component self-assembly,^[7] single-layer two-dimensional honeycomb supramolecular organic framework by multicomponent assembly,^[8] but supramolecular self-assemblies with peculiar optoelectronic properties were still rarely explored.

We herein reported the construction of microplates with optoelectronic properties. A fundamental factor for the success in fabricating this microplate was the proper combining of a

central phenanthroline unit with two terminal 4,4'-bipyridin-1-ium units in compound I (Scheme 1). The linear assembly



Scheme 1. Schematic illustration of assembly formation (Inset: TEM micrographs of nanosheets).

formed by CB[8] and I acted as building blocks for the nanolayers which further stacked to large microplates (Scheme 1).

As a typical example of the preparation, an aqueous solution of I and CB[8] in equal molar ratio ($[CB8] = [I] = 1 \times 10^{-5}$ M) was allowed to stand at 25 °C for one hour, then 20 μ L of the solution was air-dried and then subjected to transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Highly ordered microplates with square morphology were observed (Figure S1–2 and Scheme 1). The length of four edges in every microplate was same, ranging from 4.1 to 11.3 μ m. In addition to individual microplates, stacked microplates were also observed in microscopic images. These microplates possessed thinner and larger border, indicating that the molecular assembly probably proceeded through a layer-to-layer stacking. It is noteworthy that the stacking occurred between microplates in different size and horizontal swing angle, indicating that every microplate was independent from each other and could not be affected by adjacent microplates in the processing of assembly (Figure S1c–d). This deduction was confirmed by the observation of multilayer square structures with clear edges using atomic force microscopy (AFM) (Figure 1 and Figure S3a–c), and their thickness varied from 50 to 400 nm. The fine structure showed that there

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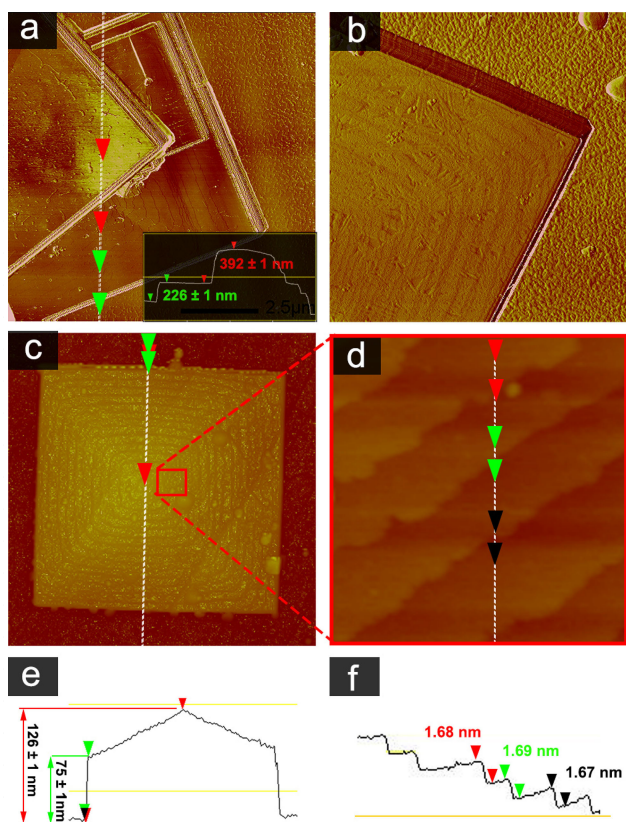


Figure 1. Tapping-mode AFM characterisation of microplates: (a) Amplitude-error image of microplate (Inset: cross-section profiles along the white dash line drawn on the image); (b) phase image of microplate; (c) 3D amplitude-error image of microplate; (d) amplitude-error image of zoomed c image; (e) cross-section profiles along the white dash line drawn on the image of c; (f) cross-section profiles along the white dash line drawn on the image of d; Samples were prepared from aqueous solution of I/CB[8] by dropping the solution on a sheet mica substrate, air-dried at 25 °C ([CB8] = [I] = 1×10^{-5} M). Note: images of (a), (b) and (c) were obtained in different areas of the sample.

existed a number of concentric shale-like arrays on the surface of multilayer square structure, and the average thickness of an individual layer (1.68 ± 0.01 nm, Figure 1f) was slightly less than the outer diameter of a CB[8] ring (1.75 nm).^[9] That was probably due to the tight stacking between layers. Moreover, the height of centre (ca. 126 ± 1 nm) was higher than that of boarder (ca. 75 ± 1 nm) of multilayer square structure with a degressive tendency (Figure 1e).

To explore the possible assembly mode of microplate, the binding of CB[8] with I in aqueous solution was investigated by ^1H NMR and UV/Vis spectroscopy. In the ^1H NMR titration experiment, the obvious upfield shifts of H_{Ar} (−0.95 ppm) and H_{a} (−0.40 ppm) as well as the slight downfield shifts of H_{b} (0.17 ppm) of a reference compound **V** was observed in the presence of CB[8] (Figure S6). Moreover, **V** gave the clear 2:1 binding stoichiometry with CB[8], and thus the binding constant between **V** and CB[8] could be calculated as $1.2 \times 10^{10} \text{ M}^{-2}$ (Figure S7). These indicated that the CB[8] cavity could strongly bind two **V** molecules. Interestingly, the Job's plot of I, which possesses two **V** units, and CB[8] gave a 1:1 binding stoichiometry, referring to either a 2:2 or a n:n intermolecular

binding mode between I and CB[8] (Figure. S5). 2D ^1H NMR diffusion-ordered spectrum (DOSY) of I/CB[8] system in D_2O ([CB8] = [I] = 1×10^{-4} M) presented the nearly identical diffusion coefficient (D) as $2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Figure S9), indicating that only one type of complex was formed in solution. Judging from the large size (464 nm) of I/CB[8] system from DLS (Figure 3c), we excluded the 2:2 binding mode, thus the I/CB[8] system should adopted an intermolecular n:n binding mode in solution to form linear supramolecular polymers (Figure S5b). It is noteworthy that the powder X-ray diffraction (XRD) pattern of I/CB[8] microplates showed the clear and sharp (001) diffraction peaks referring to layer spacing of the microplate (Figure. 2a). The characteristic reflections at $2\theta = 5.17^\circ$, $d = 17.08 \text{ \AA}$ (001), $2\theta = 10.35^\circ$, $d = 8.54 \text{ \AA}$ (002), $2\theta = 15.56^\circ$, $d = 5.69 \text{ \AA}$ (003), $2\theta = 26.11^\circ$, $d = 3.41 \text{ \AA}$ (005), and $2\theta = 31.47^\circ$, $d = 2.84 \text{ \AA}$ (006) were assigned to the layer spacing of the microplate, which was in good agreement with the average thickness of an individual layer of 1.68 nm (16.8 \AA) obtained by AFM (Figures 2d, f, and Figure 1d, f). Moreover, the characteristic

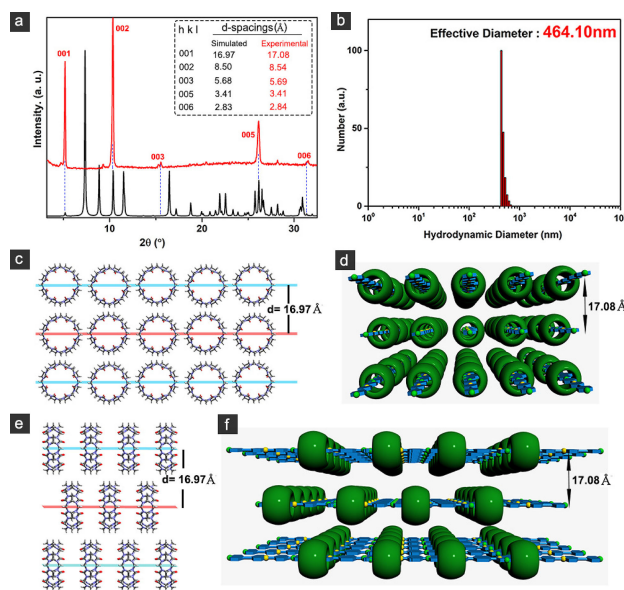


Figure 2. (a) XRD pattern of microplates. Samples were prepared from aqueous solution of I/CB[8] by dropping the solution on a glass sheet substrate, air-dried at 25 °C ([CB8] = [I] = 1×10^{-5} M). The red line is experimental data, black line is simulated data based on the crystal structure of CB[8]. (b) Dynamic light scattering (DLS) spectrum of I/CB[8] in aqueous ([I] = [CB8] = 1×10^{-4} M in aqueous after filtration by 0.8 μm filter; 25 °C; elapsed time: 5 min; angle: 90 degree). (c, e) crystal structure of CB[8] view in different directions.^[10] (d, f) Schematic representations of the microplates based on XRD data.

reflections of XRD fitted well with simulated XRD data based on the reported crystal of CB[8] (Figure 2a).^[10,11] The distances between two lattice planes were 16.97 \AA , which matched well with the XRD data of microplates of 17.08 \AA (Figure 2c and 2e). The CB[8] might arranged into one dimensional macrocycle nanotubes and further into honeycomb framework. As there were only layer spacing of the microplate, we further conducted the grazing-incidence XRD to uncover the assembly in plane. Unfortunately, there were no new peaks occurred,

which indicated that there might be some defects within layer. Although the available data did not allow us to confirm, a reasonable assembly mechanism of microplate may be as follow: firstly, the building blocks **I** and CB[8] assembled to linear supramolecular polymers through the intermolecular n:n binding; secondly, various linear supramolecular polymers integrated together to form a signal layer; thirdly, the next layer grew from the centre to the four borders on the surface of last layer to form the large square nanostructures.

Significantly, the square nanostructures exhibited the fascinating photoelectric properties. Laser scanning confocal microscopy experiments (LSCM, $\lambda_{\text{ex}}=405\text{ nm}$) showed that the square nanostructures emitted the bright and homogeneous green fluorescence (Figure 3a–c). Photophysical properties

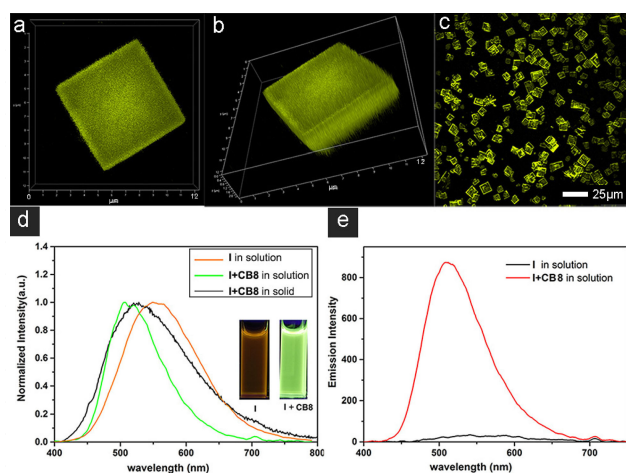


Figure 3. (a) XRD pattern of microplates. Samples were prepared from aqueous solution of **I**/CB[8] by dropping the solution on a glass sheet substrate, air-dried at 25°C ($[\text{CB8}] = [\text{I}] = 1 \times 10^{-5}\text{ M}$). The red line was experimental data, black line was simulated data based on the crystal structure of CB[8]. (b) Dynamic Light Scattering (DLS) spectrum of **I**/CB[8] in aqueous ($[\text{I}] = [\text{CB8}] = 1 \times 10^{-4}\text{ M}$ in aqueous after filtration by $0.8\text{ }\mu\text{m}$ filter; 25°C ; elapsed time: 5 min; angle: 90° degree). (c, e) crystal structure of CB[8] view in different direction.^[23] (d, f) Schematic representations of the microplates based on XRD data.

were then investigated by Fluorescence spectroscopy both in solution and solid. The aqueous of **I** displayed weak fluorescence, however, 41-fold enhanced fluorescence intensity was observed after addition of CB[8] to form as-confirmed linear supramolecular polymers (Figure 3e). To gain an insight into the reason of the fluorescence behaviors, its UV-Vis absorption spectra were examined by addition of CB[8] (Figure S4). The clear isoabsorptive point and new absorption band of 360–450 nm indicated the formation of new species. Considering the restricting effect of CB[8], this distinct bathochromic shift most probably arose from the coplanarisation of **I** induced by binding, leading to a better conjugation between its phenanthroline unit and terminal 4,4'-bipyridin-1-ium units.^[12a] The enhancement of emission and bathochromic shift of absorption spectra as described was the prototypical properties of aggregation-induced emission (AIE) effect.^[12b,13] The absolute quantum yield of **I**/CB[8] was 8.4% in the solid state, which was

nearly 4-fold higher than that of **I** (2.2%) (Table S1). This because the restriction of **I** beared was more serious in nanoplates, thus **I**/CB[8] exhibited a stronger AIE effect in solid.

As molecules with a highly planar aromatic structure were benefited to charge transportation in the solid state,^[14] the conductivity of microplates were measured. Interestingly, the microplates displayed a good conductivity under forward bias but nearly no current had been detected under reverse bias along the vertical direction (Figure 4a–c). A possible mechanism

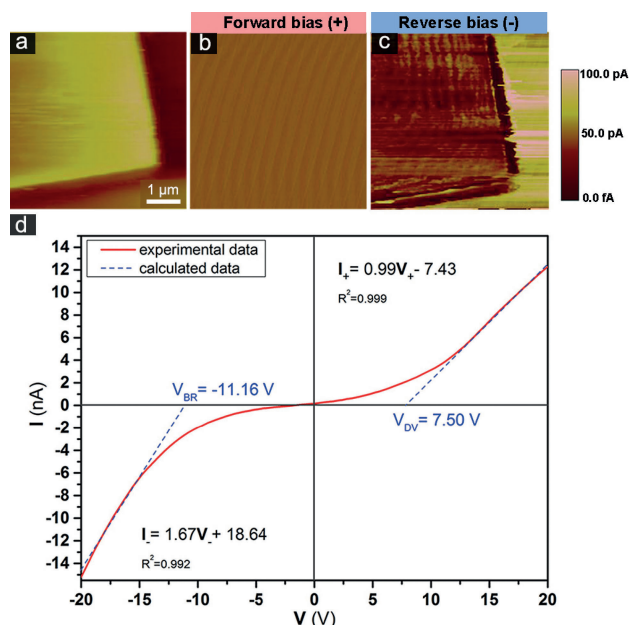


Figure 4. AFM images and I–V curve of the ambipolar semiconducting characteristics along the different directions. Contact-mode AFM amplitude-error images (a), conducting images under forward bias (b) and reverse bias (c) along the vertical direction, and I–V curve of the assemblies along the horizontal direction (d).

for this conductivity may be that the microplates could be regarded as an organic conducting charge-transfer (CT) system composed by binary **I**/CB[8] systems, in which phenanthroline units acted as donors (D) and 4,4'-bipyridin-1-ium moieties as acceptor (A). The donor and acceptor molecules alternated along the stacking directions in which π -electrons overlapped and electrons transferred between D and A molecules, thus the charge transport was most favorable along the stacking direction.^[15] As gaining effective ambipolar performance in one material without the utilizing of asymmetric was possible,^[16] the ambipolar transportation might arise from the small bandgap of the semiconductor despite of the absence of asymmetric contacts. To study the conductivity of the microplates along the horizontal direction, the microplates were prepared on gold electrodes. Nearly no ambipolar transportation could be observed on this direction, the breakdown voltage was -11.16 V and dead voltage was 7.50 V (Figure 4d). This was reasonable as **I** had a symmetrical structure. The current transportation along this direction had same circumstances.

In conclusion, a new O2D material was fabricated through multilevel supramolecular assembly and displayed peculiar optoelectronic properties by coordination assembly of cucurbit[8]uril with aromatic units and aromatic stacking between layers. The formation of assembly endowed this O2D material 41-fold fluorescence emission enhancement and anisotropic electrical properties. This work not only offered a completely understanding of self-assembly mechanism for the formation of highly regular microplates, but also provided a rapid and facile method to fabricate optoelectronic O2D nanomaterials.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: O2D • optoelectronic properties • cucurbit[8]uril • self-assembly • supramolecular chemistry

- [1] a) P. Miro, M. Audiffred, T. Heine, *Chem. Soc. Rev.* **2014**, *43*, 6537–6554; b) V. Georgakilas, M. Otyepka, A. B. Bourlino, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril, K. S. Kim, *Chem. Rev.* **2012**, *112*, 6156–6214; c) D. Chimene, D. L. Alge, A. K. Gaharwar, *Adv. Mater.* **2015**, *27*, 7261–7284.
- [2] a) T. Bauer, Z. Zheng, A. Renn, R. Enning, A. Stemmer, J. Sakamoto, A. D. Schlüter, *Angew. Chem. Int. Ed.* **2011**, *50*, 7879–7884; *Angew. Chem.* **2011**, *123*, 8025–8030; b) L. Zhang, Y. Cao, N. S. Colella, Y. Liang, J.-L. Brédas, K. N. Houk, A. L. Briseno, *Acc. Chem. Res.* **2015**, *48*, 500–509; c) D. Wu, R. Liu, W. Pisula, X. Feng, K. Müllen, *Angew. Chem. Int. Ed.* **2011**, *50*, 2791–2794; *Angew. Chem.* **2011**, *123*, 2843–2846; d) Q. An, Q. Chen, W. Zhu, Y. Li, C.-a. Tao, H. Yang, Z. Li, L. Wan, H. Tian, G. Li, *Chem. Commun.* **2010**, *46*, 725–727; e) Y. Qin, J. Zhang, X. Zheng, H. Geng, G. Zhao, W. Xu, W. Hu, Z. Shuai, D. Zhu, *Adv. Mater.* **2014**, *26*, 4093–4099.
- [3] a) W. Zhang, Y.-M. Zhang, S.-H. Li, Y.-L. Cui, J. Yu, Y. Liu, *Angew. Chem. Int. Ed.* **2016**, *55*, 11452–11456; *Angew. Chem.* **2016**, *128*, 11624–11628; b) X.-L. Ni, S. Chen, Y. Yang, Z. Tao, *J. Am. Chem. Soc.* **2016**, *138*, 6177–6183; c) A. T. Haedler, K. Kreger, A. Issac, B. Wittmann, M. Kivala, N. Hammer, J. Köhler, H.-W. Schmidt, R. Hildner, *Nature* **2015**, *523*, 196.
- [4] a) T. Fukino, H. Joo, Y. Hisada, M. Obana, H. Yamagishi, T. Hikima, M. Takata, N. Fujita, T. Aida, *Science* **2014**, *344*, 499–504; b) H.-L. Sun, Y. Chen, J. Zhao, Y. Liu, *Angew. Chem. Int. Ed.* **2015**, *54*, 9376–9380; *Angew. Chem.* **2015**, *127*, 9508–9512; c) W. Zhang, W. Jin, T. Fukushima, A. Saeki, S. Seki, T. Aida, *Science* **2011**, *334*, 340–343.
- [5] a) X. Zhuang, Y. Mai, D. Wu, F. Zhang, X. Feng, *Adv. Mater.* **2015**, *27*, 403–427; b) Y. Zheng, H. Zhou, D. Liu, G. Floudas, M. Wagner, K. Koynov, M. Mezger, H.-J. Butt, T. Ikeda, *Angew. Chem. Int. Ed.* **2013**, *52*, 4845–4848; *Angew. Chem.* **2013**, *125*, 4945–4948.
- [6] K. Ishiba, T. Noguchi, H. Iguchi, M.-a. Morikawa, K. Kaneko, N. Kimizuka, *Angew. Chem. Int. Ed.* **2017**, *56*, 2974–2978; *Angew. Chem.* **2017**, *129*, 3020–3024.
- [7] W. Bai, Z. Jiang, A. E. Ribbe, S. Thayumanavan, *Angew. Chem. Int. Ed.* **2016**, *55*, 10707–10711; *Angew. Chem.* **2016**, *128*, 10865–10869.
- [8] K.-D. Zhang, J. Tian, D. Hanifi, Y. Zhang, A. C.-H. Sue, T.-Y. Zhou, L. Zhang, X. Zhao, Y. Liu, Z.-T. Li, *J. Am. Chem. Soc.* **2013**, *135*, 17913–17918.
- [9] J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, *Acc. Chem. Res.* **2003**, *36*, 621–630.
- [10] D. Bardelang, K. A. Udachin, D. M. Leek, and J. A. Ripmeester, *CrystEng-Comm.* **2007**, *9*, 973.
- [11] Z.-W. Gao, X. Feng, L. Mu, X.-L. Ni, L.-L. Liang, S.-F. Xue, Z. Tao, X. Zeng, B. E. Chapman, P. W. Kuchel, L. F. Lindoy, G. Wei, *Dalton Trans.* **2013**, *42*, 2608–2615.
- [12] a) J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* **2001**, 1740–1741; b) Y. Zhang, T.-G. Zhan, T.-Y. Zhou, Q.-Y. Qi, X.-N. Xu, X. Zhao, *Chem. Commun.* **2016**, *52*, 7588–7591.
- [13] D. Ding, K. Li, B. Liu, B. Z. Tang, *Acc. Chem. Res.* **2013**, *46*, 2441–2453.
- [14] H. Hwang, D. Khim, J.-M. Yun, E. Jung, S.-Y. Jang, Y. H. Jang, Y.-Y. Noh, D.-Y. Kim, *Adv. Funct. Mater.* **2015**, *25*, 1146–1156.
- [15] a) L. Zhu, Y. Yi, Y. Li, E.-G. Kim, V. Coropceanu, J.-L. Brédas, *J. Am. Chem. Soc.* **2012**, *134*, 2340–2347; b) Z. G. Soos, *Annu. Rev. Phys. Chem.* **1974**, *25*, 121–153.
- [16] M. Irimia-Vladu, E. D. Głowacki, P. A. Troshin, G. Schwabegger, L. Leonat, D. K. Susarova, O. Krystal, M. Ullah, Y. Kanbur, M. A. Bodea, V. F. Razumov, H. Sitter, S. Bauer, N. S. Sariciftci, *Adv. Mater.* **2012**, *24*, 375–380.

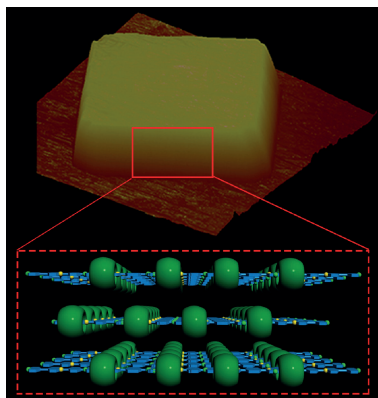
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COMMUNICATION

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1 – 5

**Organic Two-Dimensional Assembly
with Rectification Property
Mediated by Cucurbit[8]uril**



Self-assembled organic #2Dmaterials show peculiar optoelectronic properties

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