Supporting Information

The Shape-controlled Synthesis of Organometallic Microcrystal-based Hollow Hexagonal Micromotors through Evaporation-induced Supramolecular Self-assembly

Ting He,[†] Huiqiong Wu,[†] Xiaojuan Wang,[†] Qiguang Zang,[†] Peng Xue,[‡] Rujuan Shen,[§] Li Dang,[#] Yi Zhang[†]* and Juan Xiang[†]*

[†]College of Chemistry and Chemical Engineering, Central South University 932 Lushan South Road Yuelu District, Changsha, Hunan, China

Laboratory of Oil and Gas Fine Chemicals, Ministry of Education & Xinjiang Uygur Autonomous Region, Xinjiang University, Urumqi, Xinjiang 830046, China

§State Key Laboratory of Power Metallurgy Central South University 932 Lushan South Road Yuelu District, Changsha, Hunan, China

#Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, China

* E-mail: yzhangcsu@csu.edu.cn (Yi Zhang);

* E-mail: xiangj@csu.edu.cn (Juan Xiang)



Scheme S1. Synthesis of 4-CBCB (a) and Fc-Ala-BCB (b).



Figure S1 The MS spectrum of Fc-Ala-BCB.



Figure S2 The HNMR spectrum of Fc-Ala-BCB.

Table S1 Several physical parameters of acetonitrile and DMSO.

solvent	polarity	boiling point / °C
acetonitrile	6.2	82
DMSO	7.2	189



Figure S3 The optical microscopic images of microflowers composed by microrods, which were cultivated in acetonitrile/DMSO (a); The optical microscopic image of microcone consists by microrods in the 30% H₂O₂ solution and the related model (b);



Figure S4 SEM images of two microrods: the microrods present as hexagonal pyramids (a); the microrods have flat ends (b).



Figure S5 The SEM image of the spherical microflower which composed by microrods (a); The SEM image of the butterfly-like microflower which composed by microrods (b).



Figure S6 The SEM image of the microflower which composed by microrods (a); the amplified image of Figure (a).



Figure S7 The crystals are incubated by Fc-Ala-BCB solution with various concentrations: the size increased with the decreasing of the concentration.



Figure S8 The helix along the c-axis direction (a); the helix structure which is perpendicular to c-axis (b and c); the single-helix structure along the c-axis direction (d).

The molecule stacking manner obtained by DFT

Along the original crystal growth axis *c*, we can see clearly of the helix structure of Fc-Ala-BCB (Figure S9).



Figure S9.

The section of growth axis *c* presents as a delicate hexagon (Figure S10).



Figure S10

We analyzed the molecule stacking manner and find that in one original cell, there are 6 Fc-Ala-BCB molecules. Those molecules stacking along axis c by changing an angle of 149.853° (Figure S11) to form the helix structure.



Figure S11 The blue dash lines present the torsion of each two Fc-Ala-BCB molecules and numbers in blue tell the torsion angle.

There are two hydrogen bonds between nitrogen-hydrogen and ketonic oxygen (Figure S12) and one π - π stacking force between the BCB moiety and the cyclopentadienyl (Figure S13) in each two molecules. The angles of N-H---O are 160.373° and 159.868° with the N-H---O distance of 2.042 Å and 2.166 Å respectively (Figure S14).



Figure S12 Hydrogen bonds depicted as dash line in green, the number in green represents the distance between hydrogen atom and oxygen atom in unit angstrom (Å).



Figure S13 The π - π stacking between each two molecules, depicted as the white rectangle.



Figure S14 Numbers in green represent the N-H---O distance and the green dash lines represent the hydrogen bonds. Numbers in yellow represents the angle of N-H-O.



Figure S15 SEM images of the five intermediates from amorphous microspheres to the crystalline state: the incubation times are less than 4 days (a-c); the incubation times are less than 6 days (d-f).

Table S2 The calculated v	volume of the eject	ed oxygen by sto	pwatch method.
---------------------------	---------------------	------------------	----------------

The diameter of the oxygen bubble	7 µm
The volume of one oxygen bubble	38.5 μm ³
The intermediate rate of generating one bubble	2 bubble/s
The total time of catalytic reaction	508 s
The calculated volume of oxygen by stopwatch method	38.5*2*508=39.1 ml



Figure S16 The diameter of the oxygen bubble.

а 50 µm 28 °C	b 50 μm 130 °C	С 50 µm 150 °С
d	е 50 µm	f 25 μm 190 °C

Figure S17 The morphology stability of the crystals at different temperatures.