

## Supporting Information

# Temperature-responsive artificial light-harvesting system in water with tunable white-light emission

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## Table of contents

1. Materials, methods, and abbreviations.....	2
2. Synthesis of <b>M</b> .....	4
3. Self-assembly of <b>M</b> and <b>DBT@M</b> .....	6
5. Quantum yield measurements.....	8
6. Fluorescence lifetime measurements.....	9
7. Energy-transfer efficiency calculation.....	10
8. Antenna effect (AE) calculation.....	12
9. The light-harvesting behavior of <b>M</b> assembly at 50 °C.....	13
10. References.....	13

# 1. Materials, methods, and abbreviations

## General

All chemicals, reagents and solvents were purchased from commercial suppliers and used, unless otherwise stated, without further purification. If needed, solvents were dried by literature known procedures. All yields were given as isolated yields. Compound **1**<sup>[S1]</sup> and **2**<sup>[S2]</sup> were synthesized according to literature.

## NMR spectroscopy

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker AVANCE III (300 MHz) spectrometer and calibrated against the residual proton signal or natural abundance carbon resonance of the used deuterated solvent from tetramethylsilane (TMS) as the internal standard. The chemical shifts  $\delta$  are indicated in ppm and the coupling constants  $J$  in Hz. The multiplicities are given as s (singlet), m (multiplet), and br (broad).

## Mass spectrometry

High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass.

## Dynamic light scattering (DLS)

DLS measurements were carried out on a Brookhaven BI-9000AT system, equipped with a 200 mW polarized laser source ( $\lambda = 514$  nm) at a scattering angle of 90°. All samples were prepared according to the corresponding procedures mentioned above.

## Transmission electron microscope (TEM)

TEM investigations were carried out on a JEM-2100 instrument.

## Scanning electron microscopy (SEM)

SEM investigations were carried out on a ZEISS SUPRA 55 instrument.

## UV-Vis spectroscopy

The UV-Vis absorption spectra were measured on a Perkin Elmer Lambda 35 UV-Vis Spectrometer.

## **Fluorescence spectroscopy**

Fluorescence measurements were performed on an Agilent Cary Eclipse spectrofluorometer.

## **Fluorescence lifetimes**

The fluorescence lifetimes were measured employing time correlated single photon counting on a FLS980 instrument with a pulsed xenon lamp. Analysis of fluorescence decay curves were subjected to fit by a bi-exponential decay.

## **Quantum yields**

The quantum yields were carried out on a FLS980 instrument with the integrating sphere.

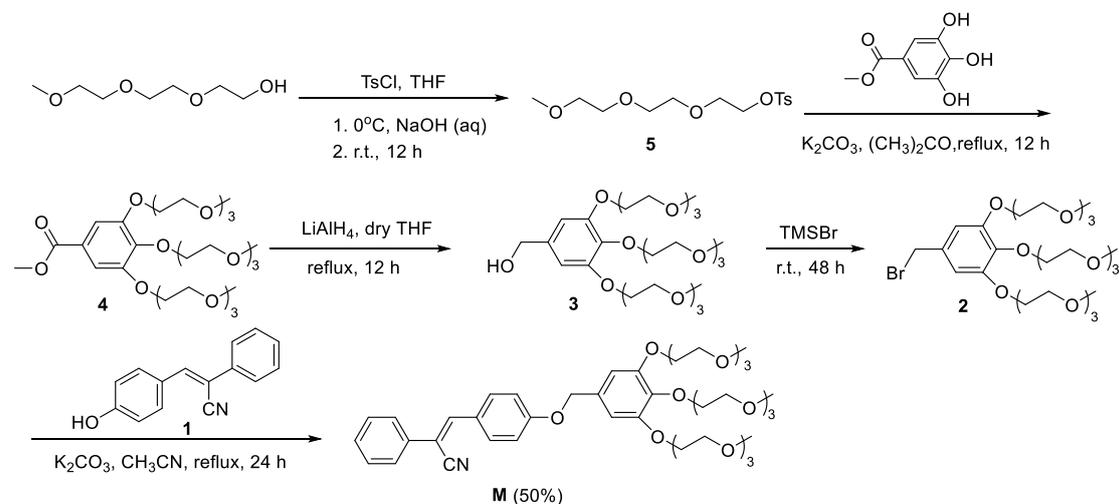
## **CIE coordinates**

The CIE (Commission Internationale de l'Eclairage) 1931 coordinates were calculated with the method of color matching functions.

## **Abbreviations**

CAC = critical aggregation concentration; NPs = nanoparticles; DCM = dichloromethane; MeOH = methanol; M = mol/L.

## 2. Synthesis of M

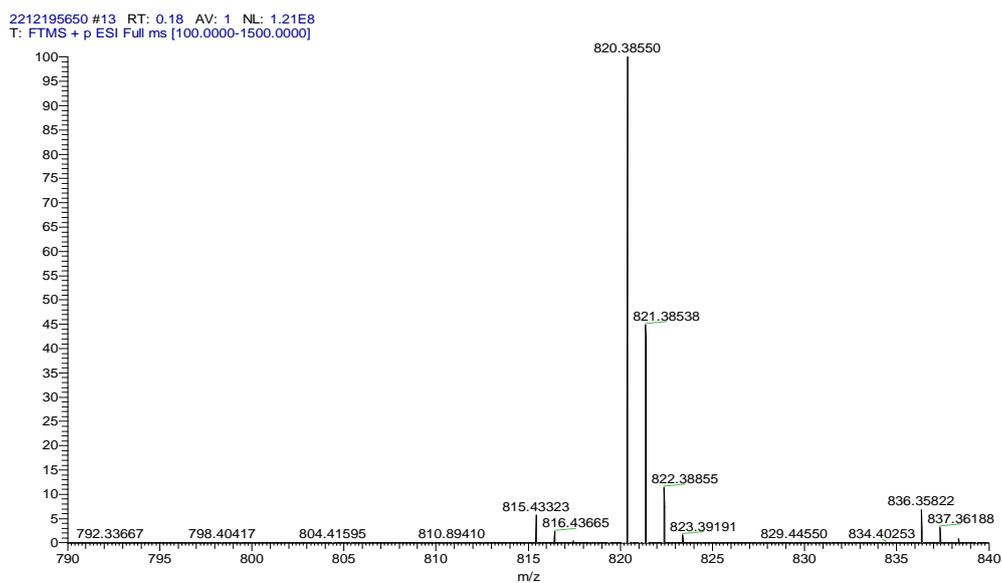


**Scheme S1.** Synthetic route of **M**. Compound **1**<sup>[S1]</sup> and compound **2**<sup>[S2]</sup> were synthesized according to the literature procedures.

### Synthesis of compound M

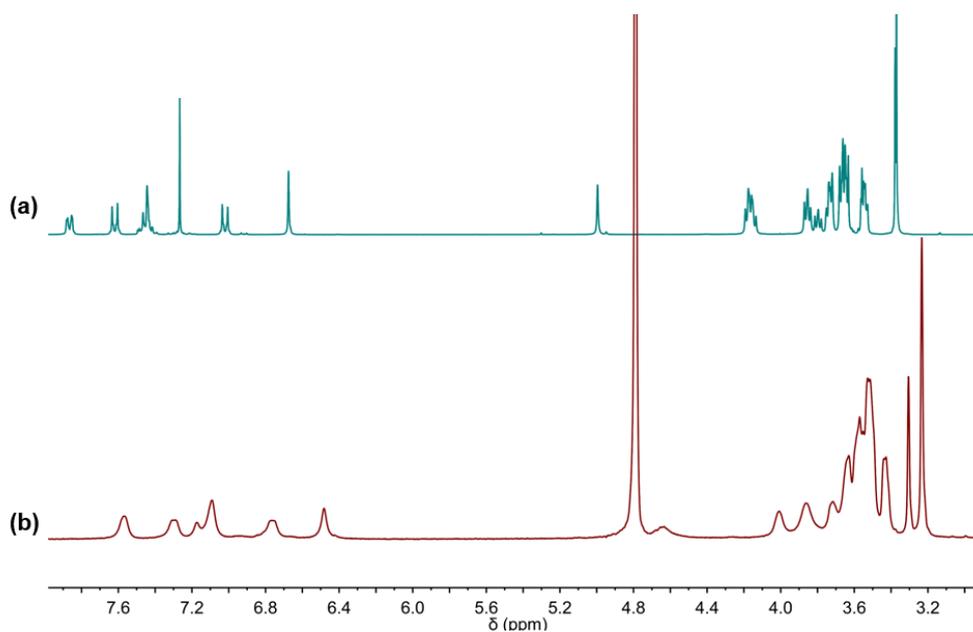
To a flask equipped with a magnetic stirrer,  $\text{K}_2\text{CO}_3$  (0.10 g, 0.72 mmol), compound **1** (0.11 g, 0.50 mmol) and acetonitrile (5 mL) were charged under  $\text{N}_2$  atmosphere. Subsequently, to the flask an acetonitrile (5 mL) solution of compound **2** (0.33 g, 0.50 mmol) was dropped slowly. The obtained mixture was refluxed for 24 h. Then the reaction mixture was cooled down to room temperature and was concentrated under reduced pressure. The crude product was purified by silica gel column chromatography ( $\text{DCM} : \text{MeOH} = 100 : 1$ , v/v) to afford compound **M** as a viscous oil (0.20 g, 0.25 mmol, 50%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298K):  $\delta$  (ppm) = 7.88-7.85 (m, 2H), 7.62 (d,  $J = 9.0$  Hz, 2H), 7.47-7.44 (m, 4H), 7.02 (d,  $J = 9.0$  Hz, 2H), 6.67 (s, 2H), 5.00 (s, 2H), 4.19-4.13 (m, 6H), 3.87-3.84 (m, 4H), 3.81-3.78 (m, 2H), 3.75-3.72 (m, 6H), 3.68-3.63 (m, 12H), 3.56-3.53 (m, 6H), 3.38-3.37 (m, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) = 159.5, 152.9, 140.3, 138.3, 134.0, 132.0, 130.2, 129.1, 128.9, 127.4, 127.3, 118.1, 115.4, 111.2, 107.1, 72.3, 72.0, 71.9, 70.8, 70.7, 70.6, 70.5, 70.2, 69.7, 68.9, 59.0. HR-ESI-MS ( $\text{C}_{43}\text{H}_{59}\text{NO}_{13}$ ):  $m/z$  calcd for  $[\text{C}_{43}\text{H}_{59}\text{NO}_{13} + \text{Na}]^+ = 820.3878$ , found = 820.3855.



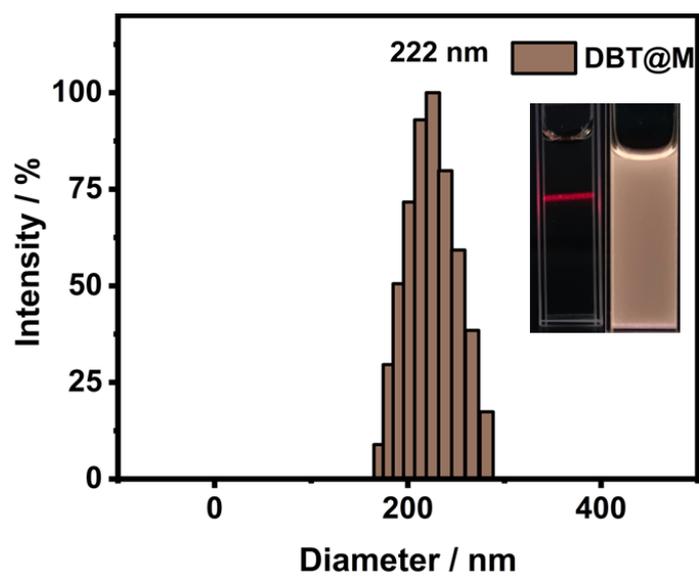


**Fig. S3.** HR-MS (ESI, positive mode, CH<sub>3</sub>OH) of **M**.

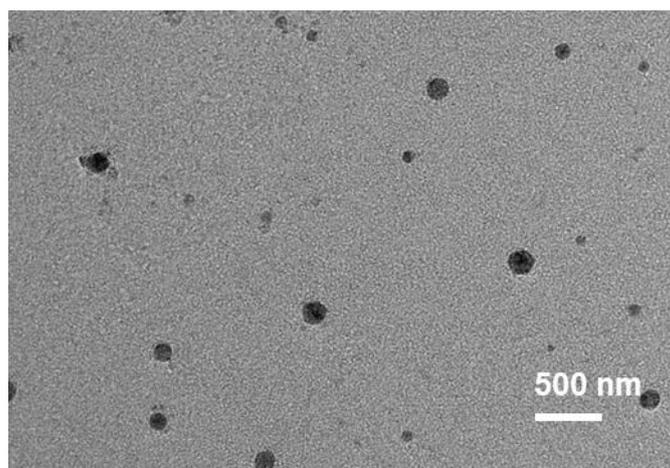
### 3. Self-assembly of **M** and DBT@**M**



**Fig. S4.** <sup>1</sup>H NMR (300 MHz, 298 K) spectra of **M** in (a) CDCl<sub>3</sub> and (b) D<sub>2</sub>O. [**M**] = 2.5 × 10<sup>-3</sup> M.

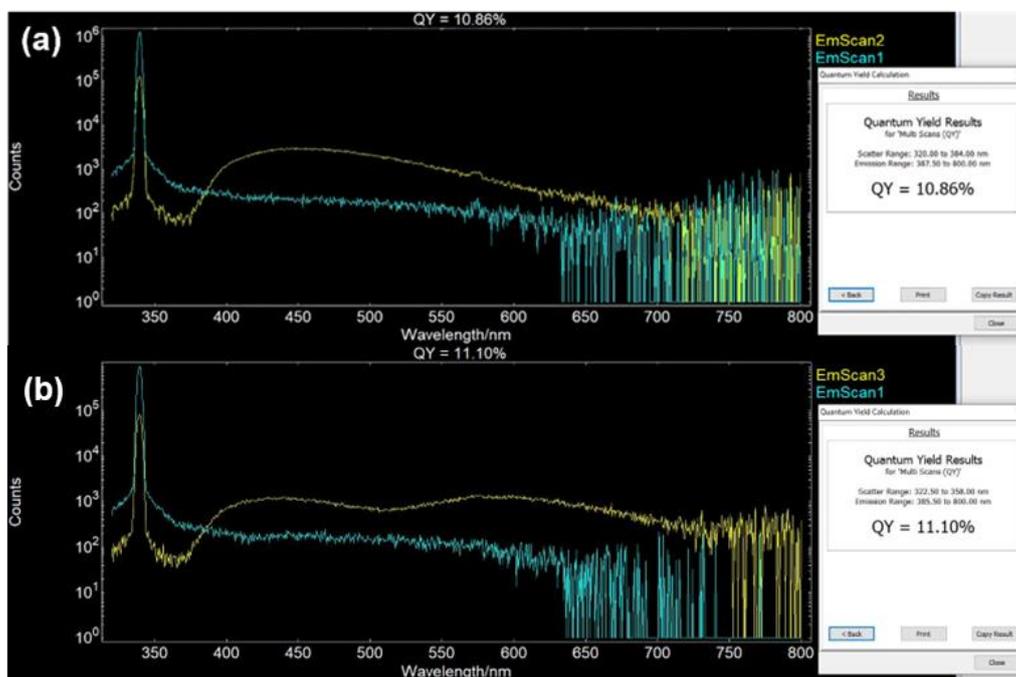


**Fig. S5.** DLS data of **DBT@M** nanoaggregates, inset: Tyndall effect and fluorescence photograph of **DBT@M**.  $[M] = 2.5 \times 10^{-4}$  M and  $[DBT] = 1.25 \times 10^{-5}$  M.



**Fig. S6.** TEM image of **DBT@M** NPs.  $[M] = 2.5 \times 10^{-4}$  M, and  $[DBT] = 1.25 \times 10^{-5}$  M, respectively.

## 5. Quantum yield measurements

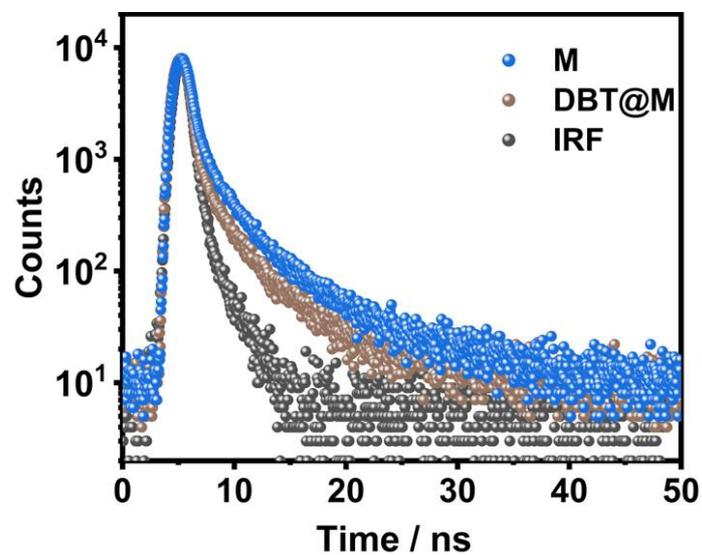


**Fig. S7.** Absolute fluorescence quantum yields ( $\Phi_{f(abs)}$ ) of (a) **M**, (b) **DBT@M** (**M:DBT** = 60:1) upon excitation at 340 nm.  $[M] = 2.5 \times 10^{-4}$  M.

**Table S1.** Fluorescence quantum yields of **M**, **DBT@M** (**M:DBT** = 20:1)  $[M] = 2.5 \times 10^{-4}$  M, and  $[DBT] = 4.2 \times 10^{-6}$  M, respectively.

Sample	Fluorescence quantum yields ( $\Phi_{f(abs)}$ )
<b>M</b>	10.86%
<b>DBT@M</b> ( <b>M : DBT = 60 : 1</b> )	11.10%

## 6. Fluorescence lifetime measurements

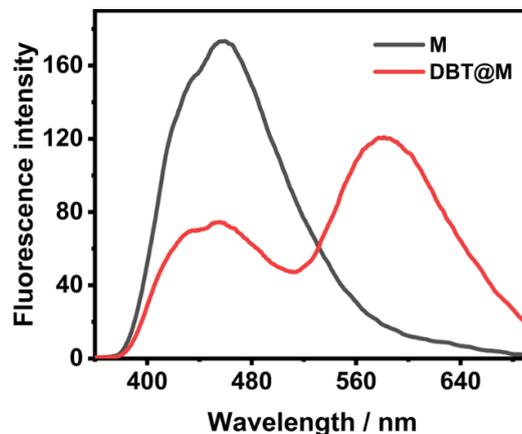


**Fig. S8.** Fluorescence decay profiles of **M** assembly (blue line) and **DBT@M** LHS ( $[\text{DBT}]/[\text{M}] = 1/20$ , brown line).

**Table S2.** Fluorescence lifetimes of **M** NPs and **DBT@M** NPs monitored at 450 nm upon excitation at 365 nm.  $[\text{M}] = 2.5 \times 10^{-4} \text{ M}$ ,  $[\text{DBT}] = 1.3 \times 10^{-5} \text{ M}$ , respectively.

Sample	$\tau_1/\text{ns}$	RW1[%]	$\tau_2/\text{ns}$	RW2[%]	$\tau/\text{ns}$	$\chi^2$
<b>M</b>	2.36	52.8	8.55	47.2	5.27	1.17
<b>DBT@M</b> ( <b>M</b> : <b>DBT</b> = 20 : 1)	2.03	54.3	7.31	45.7	4.44	1.16

## 7. Energy-transfer efficiency calculation



**Fig. S9.** Fluorescence spectra of **M** and **DBT@M** assembly upon excitation at 340 nm. **M** (black line), **DBT@M** (red line), respectively.  $[M] = 2.5 \times 10^{-4}$  M,  $[DBT] = 1.25 \times 10^{-5}$  M, respectively.

Energy-transfer efficiency ( $\Phi_{ET}$ ) was calculated from fluorescence spectra through the equation S1<sup>[S3]</sup>:

$$\Phi_{ET} = 1 - I_{DA}/I_D \text{ (eq. S1)}$$

Where  $I_{DA}$  and  $I_D$  are the fluorescence intensities of **DBT@M** (donor and acceptor) and **M** (donor) at 450 nm when excited at 340 nm, respectively.

The energy-transfer efficiency ( $\Phi_{ET}$ ) was calculated as 56.9% in water, measured under the condition of  $[M] = 2.5 \times 10^{-4}$  M,  $[DBT] = 1.25 \times 10^{-5}$  M, respectively,  $\lambda_{ex} = 340$  nm.

**Table S3.** Energy-transfer efficiency with different donor/acceptor ratio of **DBT@M**.

Sample	Concentration, respectively	Energy-transfer efficiency ( $\Phi_{ET}$ )
<b>DBT@M</b> ( <b>DBT@M</b> = 20:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 1.3 \times 10^{-5}$ M	56.9%
<b>DBT@M</b> ( <b>DBT@M</b> = 60:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 4.2 \times 10^{-6}$ M	43.9%
<b>DBT@M</b> ( <b>DBT@M</b> = 75:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 3.3 \times 10^{-6}$ M	40.3%
<b>DBT@M</b> ( <b>DBT@M</b> = 100:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 2.5 \times 10^{-6}$ M	31.0%
<b>DBT@M</b> ( <b>DBT@M</b> = 300:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 8.3 \times 10^{-7}$ M	21.5%

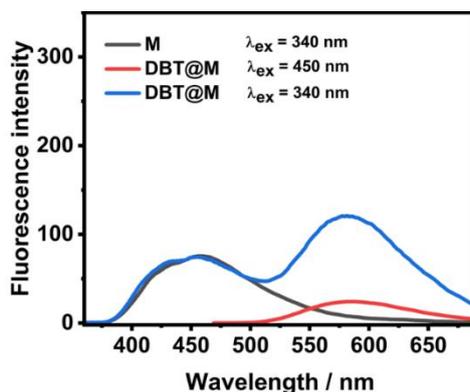
According to literature<sup>[S4]</sup>, the energy-transfer efficiency can be also calculated from the fluorescence lifetimes of the donor in the absence and presence of the acceptor by employing the following equation:  $\Phi'_{ET} = 1 - \tau_{DA}/\tau_D$ , where  $\tau_{DA}$  and  $\tau_D$  are the fluorescence lifetimes of NPs of **DBT@M** (donor and acceptor) and NPs of **M** (only donor), respectively. According to the lifetime data listed in Table S2,  $\Phi'_{ET}$  was calculated to be 15.7% (**M/DBT** = 20/1), which is lower than  $\Phi_{ET}$  calculated from fluorescence intensity data. The different values might be due to different spectroscopies, which is also observed and discussed by other researchers (*Nanoscale*, 2019, **11**, 16284.). Moreover, we found many supramolecular light-harvesting systems showed dramatic differences in  $\Phi_{ET}$  (calculated from steady-state fluorescence) and  $\Phi'_{ET}$  (Table R1). In previous reported artificial light-harvesting systems, most of them expressed energy-transfer efficiency from steady-state fluorescence intensity data. However, they also reported fluorescence decay data. Therefore, we can calculate  $\Phi'_{ET}$  from these decay data, as showed in Table S4. From these data, we can see that energy transfer in FRET of supramolecular system is a complicated phenomenon. Although the energy transfer process is complicated, which may include FRET and potential radiant energy transfer, the acceptor (**DBT**) in our system is still efficient in capturing energy from donor and exhibits strong luminescence.

**Table S4.** Energy transfer efficiency reported by literatures.

Entry	System	$\Phi_{ET}$	$\Phi'_{ET}$	Ref.
1	DBT@M (D/A = 20/1)	56.9%	15.7%	This paper.
2	Zn-1 $\rightarrow$ EY	82.4%	3.8%	<i>Chem. Sci.</i> 2023, <b>14</b> , 2237.
3	LHCII-TR (0.2 $\mu$ M/6.8 $\mu$ M)	64.5%	32.7%	<i>Nanoscale</i> , 2019, <b>11</b> , 16284.
4	WP6-G-NiR (D/A = 150/1)	55.0%	34.5%	<i>Angew. Chem. Int. Ed.</i> , 2018, <b>57</b> , 3163.
5	WP5-TPEDA-ESY (D/A = 200/1)	74.4%	58.7%	<i>Angew. Chem. Int. Ed.</i> , 2020, <b>59</b> , 10095.
6	NPS-SC4AD-NiB (D/A = 250/1)	60.8%	16.7%	<i>Angew. Chem. Int. Ed.</i> , 2020, <b>59</b> , 10493.
7	Cage 4b-ESY (D/A = 19/1)	45.0%	8.3%	<i>Angew. Chem. Int. Ed.</i> , 2019, <b>131</b> , 8954.
8	WP5-BPT-DBT (D/A = 350/1)	60.9%	35.0%	<i>J. Mater. Chem. A.</i> , 2020, <b>8</b> , 9590.
9	TPE-CHO-TPE-TCF (D/A = 100/1)	95.0%	73.6%	<i>Angew. Chem. Int. Ed.</i> , 2019, <b>58</b> , 1643.
10	OPV-I-SCD-NiR (D/A = 125/1)	72.0%	49.1%	<i>Adv. Mater.</i> , 2017, <b>29</b> , 1701905.
11	PPTA-WP5-EY (D/A = 20/1)	67.0%	32.9%	<i>ACS Appl. Mater. Interfaces</i> 2022, <b>14</b> , 45734.
12	TG1-ESY (D/A = 3/1)	42.5%	23.2%	<i>Angew. Chem. Int. Ed.</i> , 2021, <b>60</b> , 18761.

Note:  $\Phi_{ET}$  generally was exhibited in the literature text.  $\Phi'_{ET}$  was calculated from the fluorescence lifetime provided in the literatures.

## 8. Antenna effect (AE) calculation



**Fig. S10.** Fluorescence spectrum of **M** and **DBT@M** normalized at 450 nm, **M** (black line), **DBT@M** (blue line), respectively,  $\lambda_{ex} = 340$  nm. The red line represents the fluorescence spectrum of **DBT@M**,  $\lambda_{ex} = 450$  nm.  $[M] = 2.5 \times 10^{-4}$  M, and  $[DBT] = 1.3 \times 10^{-5}$  M, respectively.

The antenna effect (AE) was calculated based on the emission spectra using equation S2<sup>[S3]</sup>:

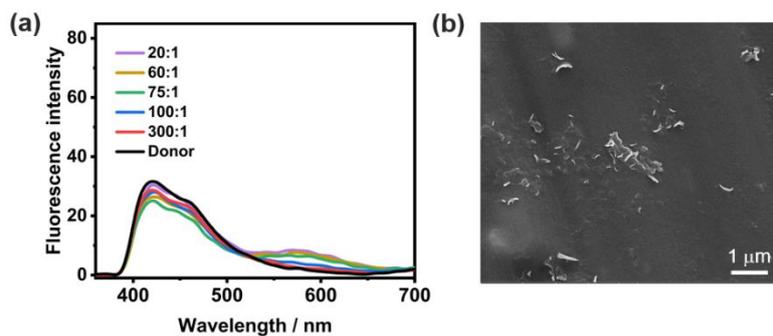
$$AE = I'_{DA,340}/I_{DA,450} = (I_{DA,340} - I_{D,340})/I_{DA,450} \text{ (eq. S2)}$$

Where  $I_{DA,340}$  and  $I_{DA,450}$  are the fluorescence intensities at 580 nm with the excitation of the light-harvesting NPs at 340 nm and at 450 nm, respectively.  $I_{D,340}$  refers to the fluorescence intensity of **DBT@M** NPs at 580 nm under excitation at 340 nm after its emission spectrum being normalized at 450 nm with the black line. The antenna effect value was calculated as 4.7 in water, measured under the condition of  $[M] = 2.5 \times 10^{-4}$  M, and  $[DBT] = 1.3 \times 10^{-5}$  M, respectively.

**Table S5.** Antenna effect with different donor/acceptor ratios of **DBT@M**.

Sample	Concentration, respectively	Antenna Effect (AE)
<b>DBT@M</b> ( <b>DBT@M</b> = 20:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 1.3 \times 10^{-5}$ M	4.7
<b>DBT@M</b> ( <b>DBT@M</b> = 60:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 4.2 \times 10^{-6}$ M	6.2
<b>DBT@M</b> ( <b>DBT@M</b> = 75:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 3.3 \times 10^{-6}$ M	6.2
<b>DBT@M</b> ( <b>DBT@M</b> = 100:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 2.5 \times 10^{-6}$ M	7.6
<b>DBT@M</b> ( <b>DBT@M</b> = 300:1)	$[M] = 2.5 \times 10^{-4}$ M $[DBT] = 8.3 \times 10^{-7}$ M	7.4

## 9. The light-harvesting behavior of M assembly at 50 °C



**Fig. S11.** (a) Fluorescence spectra of **M** in water with different concentrations of **DBT** at 50 °C. (b) SEM images of **DBT@M** prepared from a turbid solution at 50 °C

## 10. References

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- [S4] Peng, H.-Q.; Niu, L.-Y.; Chen, Y.-Z.; Wu, L.-Z.; Tung, C.-H.; Yang, Q.-Z., *Chem. Rev.* **2015**, *115*, 7502-7542.