Electronic Supplementary Information

An efficient artificial light-harvesting system with tunable emission in water constructed from H-bonded AIE supramolecular polymer and Nile Red

Tangxin Xiao,*^a Haoran Wu,^a Guangping Sun,^b Kai Diao,^a Xiaoyan Wei,^a Zheng-Yi Li,^a Xiao-

Qiang Sun,^a Leyong Wang,^{a,b}

^aSchool of Petrochemical Engineering, Changzhou University, Changzhou, 213164, China. ^bSchool of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210023, China.

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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.

NMR spectroscopy

The ¹H NMR and ¹³C 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 δ are indicated in ppm and the coupling constants *J* in Hz. The multiplicities are given as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), and m (multiplet).

Mass spectrometry

Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on LCMS2020. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass.

Scanning electron microscopy (SEM)

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

Transmission electron microscope (TEM)

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

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.

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 a mono-exponential or bi-exponential decay. The instrument response function (IRF) measures the scattering of laser excitation from non-fluorescent control samples to determine the fastest possible response of the detectors.

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.

Viscometry

Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298 K in chloroform and acetonitrile.

Abbreviations

UPy = 2-ureido-4[1H]-pyrimidinone; THF = Tetrahydrofuran; NPs = nanoparticles

DCM = dichloromethane; M = mol/L; br = broad; Ar = aromatic group

2. Specific viscosity of 1



Fig. S1. Specific viscosity of **1** in DCM solutions versus the concentration (298 K). Values on the curves indicate the slope.



3. Fluorescence lifetime measurements

Fig. S2. Fluorescence decay profiles of (a) other 1-NiR NPs (D:A = 150/1, 250/1, 400/1, 750/1, and 1500/1 ($\lambda_{em} = 480 \text{ nm}$), and (b) 1-NiR NPs at D:A = 100/1 and NiR NPs in water ($\lambda_{em} = 595 \text{ nm}$). [1] = 5×10⁻⁵ M.

Although the intensity of the emission spectrum of **NiR** (acceptor) in the form of NPs in water is very weak due to ACQ (Fig. S8), the fluorescence lifetime is still measurable (Fig. S2b). Compared with **1-NiR**, the average fluorescence lifetime of **NiR** was measured to be 2.50 ns (Table S2), indicating that the lifetime of acceptor was indeed increased in **1-NiR**. The increase in lifetime of **NiR** and decrease in lifetime of **1** in donor-acceptor system may suggest that trivial energy transfer in the system might be negligible.

Sample	$ au_1/ns$	RW1 [%]	τ_2/ns	RW2 [%]	τ/ns	χ²
1	3.67	36.7	8.14	63.3	6.50	1.060
1-NiR (1 : NiR = 100 : 1)	2.73	75.4	6.72	24.6	3.71	1.149
1-NiR (1 : NiR = 150 : 1)	2.23	5.7	4.00	94.3	3.90	1.180
1-NiR (1 : NiR = 250 : 1)	3.38	51.1	5.24	48.9	4.29	1.112
1-NiR (1 : NiR = 400 : 1)	4.72	100	-	-	4.72	1.022
1-NiR (1 : NiR = 750 : 1)	5.42	100	-	-	5.42	0.935
1-NiR (1 : NiR = 1500 : 1)	6.16	100	-	-	6.16	0.973

Table S1. Fluorescence lifetimes of NPs of **1** and different **1-NiR** NPs upon excitation at 365 nm in aqueous solution, $[1] = 5 \times 10^{-5}$ M.

Note: Fluorescence decay curves of **1** and **1-NiR** (100/1, 150/1, 250/1) were subjected to fit a biexponential decay. Fluorescence decay curves of **1-NiR** (400/1, 750/1, 1500/1) were subjected to fit a mono-exponential decay.

Table S2. Fluorescence lifetimes of **1-NiR** NPs (D:A = 100/1) and **NiR** upon excitation at 365 nm in aqueous solution, $[1] = 5 \times 10^{-5}$ M, $[NiR] = 5 \times 10^{-7}$ M, respectively.

Sample	τ_1/ns	RW1 [%]	τ_2/ns	RW2 [%]	τ/ns	χ^2
NiR	0.66	15.2	2.83	84.8	2.50	0.984
1-NiR (1 : NiR = 100 : 1)	1.77	26.3	3.94	73.7	3.37	1.041

4. Quantum yield measurements





(b)



(c)



Fig. S3. Absolute fluorescence quantum yields ($\Phi_{f(abs)}$) of (a) NPs of **1**, (b) NPs of **1-NiR** (**1/NiR** = 100/1), and (c) NPs of **1-NiR** (**1/NiR** = 250/1), upon excitation at 365 nm in aqueous solution. [**1**] = 5×10^{-5} M.

Sample	Fluorescence quantum yields			
Sampe	$(\mathbf{\Phi}_{\mathrm{f(abs)}})$			
1	80.12%			
1-NiR (1 : NiR = 100 : 1)	58.71%			
1-NiR (1 : NiR = 250 : 1)	14.81%			

Table S3. Fluorescence quantum yields of NPs of **1** and **1-NiR**. $[1] = 5 \times 10^{-5}$ M, $[NiR] = 5 \times 10^{-7}$ M, respectively.

5. Energy-transfer efficiency calculation



Fig. S4. (a)~(f) Fluorescence spectra of **1** and different ratio of **1-NiR** assembly upon excitation at 365 nm.

Notably, the absorption of the acceptor (**NiR**) at the donor excitation wavelength (365 nm) was negligible, especially at low acceptor concentrations (a maximum of 1 mol% was used during the experiment), which ruled out the possibility for direct excitation of the acceptor on excitation of the donor (Fig. S5). It should be noting that the absorption spectrum of **NiR** in Fig. 3a was normalized. As shown in Fig. S5, the actual absorption intensity of **NiR** ([**NiR**] = 10^{-7} M) is relatively very low when 1/NiR = 100/1 ([1] = 10^{-5} M). The effect is more negligible when the quantity of **NiR** is reduced.



Fig. S5. Absorption spectrum of 1 and NiR in water. $[1] = 5 \times 10^{-5}$ M, $[NiR] = 5 \times 10^{-7}$ M.

Furthermore, the emission residue of **NiR** should be negligible on the calculation of energy transfer efficiency. As shown in Fig. S6, **NiR** itself in NPs in water showed no emission (blue line). This should be due to its ACQ property in NPs without the help of **1**. Instead, we measured it in apolar solvent DCM in mimicking the hydrophobic environment of it inside the **1-NiR** NPs. The emission spectrum of **NiR** in DCM (yellow line) was normalized at 595 nm with the **NiR** emission in **1-NiR** (D/A=100/1). It can be clearly seen that **NiR** has no emission residue at 480 nm because no emission can be observed when it reaches 530 nm. Although this is slightly different from the actual emission of **NiR** in NPs in water, plus the actual emission peak shape (red line, 550 nm - 650nm), it can be basically concluded that **NiR** has no emission residue at 480 nm in the D/A system. As a result, the emission residue of **NiR** should be negligible on the calculation of energy transfer efficiency. Moreover, the emission residue of **NiR** is more negligible when the concentration of the **NiR** is further reduced (from D/A =150/1 to 1500/1).



Fig. S6. Emission spectrum of **1** ([**1**] = 5×10^{-5} M), **1-NiR** NPs ([**1**] = 5×10^{-5} M, [**NiR**] = 5×10^{-7} M), **NiR** NPs ([**NiR**] = 5×10^{-7} M) in water, and **NiR** ([**NiR**] = 5×10^{-7} M) in DCM. $\lambda_{ex} = 365$ nm.

Energy-transfer efficiency (Φ_{ET}) was calculated from fluorescence spectra through the equation S1^[S1]:

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

Where I_{DA} and I_D are the fluorescence intensities of NPs of 1-NiR (donor and acceptor) and NPs of 1 (donor) at 480 nm when excited at 365 nm, respectively.

Table S4. Energy-transfer efficiency wit	th different D/A ratio
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Sample	Concentration, respectively	Energy-transfer efficiency $(\Phi_{ ext{ET}})$	
1 NPD (1 . NPD 100 . 1)	$[1] = 5 \times 10^{-5} \text{ M}$	92.40/	
1-NIK (1 : NIK = $100 : 1$)	$[NiR] = 5 \times 10^{-7} M$	82.4%	
1 N;D $(1 \cdot N;D - 150 \cdot 1)$	$[1] = 5 \times 10^{-5} \text{ M}$	68.00/	
1-INIK (1 . INIK $= 150 \cdot 1$)	$[NiR] = 3.33 \times 10^{-7} M$	08.070	
1 NiP $(1 \cdot NiP - 250 \cdot 1)$	$[1] = 5 \times 10^{-5} \text{ M}$	53 104	
1-1000 (1.1000 - 250.1)	$[NiR] = 2 \times 10^{-7} M$	33.470	
1-NiP $(1 \cdot NiP - 400 \cdot 1)$	$[1] = 5 \times 10^{-5} \text{ M}$	40 7%	
1-101K(1.101K - 400.1)	$[NiR] = 1.25 \times 10^{-7} M$	40.770	
1-NiR (1 · NiR – 750 · 1)	$[1] = 5 \times 10^{-5} \text{ M}$	26.2%	
1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 +	$[NiR] = 6.67 \times 10^{-8} M$	20.270	
1-NiR $(1 \cdot NiR = 1500 \cdot 1)$	$[1] = 5 \times 10^{-5} \text{ M}$	10.2%	
$1 = 1000 \cdot 1$	$[NiR] = 3.33 \times 10^{-8} M$	10.270	

Energy-transfer efficiency could be also calculated from fluorescence lifetime by employing the following equation: $\Phi_{ET} = 1 - \tau_{DA} / \tau_D$ (eq. S2), where τ_{DA} and τ_D are the fluorescence lifetimes of NPs of 1-NiR (donor and acceptor) and NPs of 1 (donor) when excited at 365 nm, respectively. According to the lifetime data listed in Table S1, Φ_{ET} was calculated to be 42.9% (1/NiR = 100/1), 40.0% (1/NiR = 150/1), 34.0% (1/NiR = 250/1), 27.4% (1/NiR = 400/1), 16.6% (1/NiR = 750/1), 5.2% (1/NiR = 1500/1). Although the values are different, energy transfer efficiency calculated

from time-resolved and steady-state data show good agreement of the trend. The different values might be due to different spectroscopies, which is also observed and discussed by other researchers ^[2]. Moreover, we found many supramolecular light-harvesting systems showed dramatic differences in Φ_{ET} (calculated from steady-state fluorescence) and Φ'_{ET} (Table S5). 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 (NiR) in our system is still more efficient in capturing energy from donor and exhibits strong luminescence, which is the main purpose of this work, resulting in higher antenna effects and color-tunable luminescent materials.

Entry	System	Фет	Φ'ετ	Ref.
1	1-NiR (D/A = 100/1)	82%	43%	This paper.
2	1-NiR (D/A = 150/1)	68%	40%	This paper.
3	LHCII-TR (0.2uM/6.8uM)	64%	32%	Nanoscale, 2019, 11 , 16284-16292.
4	WP6-G-NiR (D/A = 150/1)	55%	34%	Angew. Chem. Int. Ed., 2018, 57, 3163-3167.
5	WP5-TPEDA-ESY (D/A = 200/1)	74%	59%	Angew. Chem. Int. Ed., 2020, 59, 10095-10100.
6	NPS-SC4AD-NiB (D/A = 250/1)	61%	17%	Angew. Chem. Int. Ed., 2020, 59 , 10493-10497.
7	Cage 4b-ESY (D/A = 19/1)	45%	7%	Angew. Chem. Int. Ed., 2019, 131, 8954-8958
8	WP5-BPT-DBT (D/A = 350/1)	61%	35%	J. Mater. Chem. A., 2020, 8, 9590-9596.
9	Py-TPE-WP5-SR101 (D/A = 150/1)	64%	44%	Chem. Commun., 2020. 56. 5949-5952.
10	Py-TPE-WP5-ESY (D/A = 150/1)	84%	55%	Chem. Commun., 2020. 56. 5949-5952.
11	TPE-CHO-TPE-TCF (D/A = 100/1)	95%	74%	Angew. Chem. Int. Ed., 2019, 58, 1643-1647.
12	OPV-I-SCD-NiR (D/A = 125/1)	72%	49%	Adv. Mater., 2017, 29 , 1701905.

Table S5. Energy transfer efficiency reported by literatures.

Note: Φ_{ET} generally was exhibited in the literature text. Φ'_{ET} was calculated from the fluorescence lifetime provided in the literatures.

6. Antenna effect (AE) calculation



Fig. S7. (a)~(f) Fluorescence spectra of different ratio of 1-NiR (red line), blue line (acceptor emission, $\lambda_{ex} = 480$ nm). The black line represents the fluorescence spectrum of 1, which was normalized according to the fluorescence intensity at 480 nm of the red line.

The antenna effect (AE) was calculated based on the emission spectra using equation S3^[S1]:

$$\mathbf{AE} = \mathbf{I'}_{\mathbf{DA},365} / \mathbf{I}_{\mathbf{DA},480} = (\mathbf{I}_{\mathbf{DA},365} - \mathbf{I}_{\mathbf{D},365}) / \mathbf{I}_{\mathbf{DA},480} \text{ (eq. S3)}$$

Where $I_{DA,365}$ and $I_{DA,480}$ are the fluorescence intensities at 595 nm with the excitation of the light-harvesting NPs at 365 nm and at 480 nm, respectively. $I_{D,365}$ is the fluorescence intensities at 595 nm of the NPs of **1**, which was normalized with the **1-NiR** assembly at 480 nm.

Notably, the true emission intensity ($I'_{DA,365}$) of the acceptor (NiR) at 595 nm in the lightharvesting system should be corrected by subtracting the emission residue of the donor at 595 nm ($I_{D,365}$, black line in Fig. S7, which was normalized at 480 nm for each spectrum) and the emission of the acceptor itself ($I_{A,365}$) at 595 nm ($\lambda_{ex} = 365$ nm). Thus, $I'_{DA,365} = I_{DA,365} - I_{D,365} - I_{A,365}$. As shown from Fig. S5, the absorption of the acceptor at the donor excitation wavelength (365 nm) was negligible. Thus, the emission of the acceptor itself ($\lambda_{ex} = 365$ nm) was also negligible. Therefore, $I_{A,365}$ should be negligible. As a result, the true emission intensity of the acceptor (NiR) at 595 nm in the light-harvesting system was $I'_{DA,365} = I_{D,365} - I_{D,365}$.



Fig. S8. Emission spectrum of **1** ([**1**] = 5×10^{-5} M), **1-NiR** ([**1**] = 5×10^{-5} M, [**NiR**] = 5×10^{-7} M), and **NiR** ([**NiR**] = 5×10^{-7} M) as NPs in water. $\lambda_{ex} = 365$ nm.

Table S6.	Antenna	effect v	vith	different	donor	acceptor ratio.	
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Sample	Concentration, respectively	Antenna Effect (AE)	
1 N:D (1 . N:D 100 . 1)	$[1] = 5 \times 10^{-5} \text{ M}$		
1-NIK (1 : NIK = $100 : 1$)	$[NiR] = 5 \times 10^{-7} M$	15.5	
1 N; D $(1 \cdot N; D - 150 \cdot 1)$	$[1] = 5 \times 10^{-5} \text{ M}$	22.2	
$1^{-1}(100, 100, 100, 100, 100, 100, 100, 100,$	$[NiR] = 3.33 \times 10^{-7} M$	22.2	
1.NiP $(1 \cdot NiP - 250 \cdot 1)$	$[1] = 5 \times 10^{-5} \text{ M}$	28.0	
$1^{-1}(\mathbf{K}(1,1)\mathbf{K}-250,1)$	$[NiR] = 2 \times 10^{-7} M$	28.0	
1-NiR $(1 \cdot NiR - 400 \cdot 1)$	$[1] = 5 \times 10^{-5} \text{ M}$	30.5	
1 - 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 +	$[NiR] = 1.25 \times 10^{-7} M$	50.5	
1.NiR (1 · NiR – 750 · 1)	$[1] = 5 \times 10^{-5} \text{ M}$	32.9	
1 - 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 +	$[NiR] = 6.67 \times 10^{-8} M$		
1.NiR (1 · NiR – 1500 · 1)	$[1] = 5 \times 10^{-5} \text{ M}$	29.4	
1 -14 1 (1 - 14 1 1 - 1500 · 1)	$[NiR] = 3.33 \times 10^{-8} M$	27.7	

7. Control experiment of compound 5 for light-harvesting



Fig. S9. (a) Fluorescence spectra of **1** and **1-NiR** upon excitation at 365 nm. (b) Fluorescence spectra of compound **5** and **5-NiR** upon excitation at 365 nm. All these compounds are existed as NPs in water. $[\mathbf{1}] = 5 \times 10^{-5} \text{ M}, [\mathbf{5}] = 5 \times 10^{-5} \text{ M}, [\mathbf{NiR}] = 5 \times 10^{-7} \text{ M}$, respectively.

8. Synthesis of 1



Scheme S1. Synthesis of 1

Compound **5** was synthesized via McMurry coupling reaction according to literature.^[S2] To a flask equipped with a magnetic stirrer, zinc powder (7.18 g, 109.8 mmol) and THF (100 mL) were charged under an argon atmosphere. This mixture was cooled to 0 °C, and then TiCl₄ (10.43 g, 55.0 mmol) was dropwise added. The system was refluxed for 2.5 h and cooled to 0 °C and then *p*-methoxybenzophenone (5.80 g, 27.4 mmol) dissolved in THF (30 mL) was dropwise added into the system. The mixture was refluxed overnight. The mixture was cooled down to room temperature and the reaction was quenched by the addition of saturated aqueous solution of NaHCO₃, until no bubbles were released. The reacted mixture was extracted with DCM (100 mL × 3). The organic layer was dried with anhydrous MgSO₄. With rotary evaporation, the crude product was obtained, which was purified by recrystallization with DCM and hexane to afford compound **5** as a white solid (4.6 g, 11.7 mmol). Yield: 85 %. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.12-7.01 (m, 10H, Ar*H*), 6.69-6.90 (m, 4H, Ar*H*), 6.67-6.60 (m, 4H, Ar*H*), 3.75-3.73 (m, 6H, OC*H*₃). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 157.9, 144.3, 139.6, 136.4, 132.6, 131.4, 127.6, 126.2, 113.0, 55.1.



Fig. S10. ¹H NMR spectrum (300 MHz, CDCl₃, 298 K) of compound 5.



Fig. S11. ¹³C NMR spectrum (75 MHz, CDCl₃, 298 K) of compound 5.

Synthesis of compound 4^[S3]

To a flask equipped with a magnetic stirrer, compound **5** (4.00 g, 10.2 mmol) and DCM (200 mL) were charged under an argon atmosphere. The mixture was cooled to 0 °C and then BBr₃ (6.26 g, 25.0 mmol) was added with vigorous stirred over 15 min. After the system was warmed to room temperature, the reaction was stirred overnight. The flask was then immersed into an ice-water bath and water (50 mL) was dropwise added. The reacted mixture was extracted with DCM (100 mL \times 3). The organic layer was isolated and washed with water three times. The organic layer was dried with anhydrous MgSO₄. With rotary evaporation, the crude product was obtained, which was purified by recrystallization with EtOH and water to afford compound **4** as a white solid (3.30 g, 9.0 mmol). Yield: 88 %. The product was used directly in the next step.

To a flask equipped with a magnetic stirrer, compound **4** (3.30 g, 9.0 mmol), K₂CO₃ (3.74 g, 27.0 mmol), and DMF (100 mL) were charged under an argon atmosphere. The mixture was stirred at room temperature for 0.5 h. The *N*-(3-bromopropyl)phthalimide (6.00 g, 22.6 mmol) was added into the mixture. The mixture was stirred at 80 °C overnight. After the system was cooled to room temperature and the reaction was quenched by adding water. The reacted mixture was extracted with DCM (100 mL × 3). The organic layer was dried with anhydrous MgSO₄. The crude product was purified by silica gel chromatography (PE : DCM = 1 : 1, ν/ν) to afford compound **3** as a light yellow solid (4.83 g, 6.5 mmol). Yield: 72 %. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.84-7.81 (m, 4H, Ar*H*), 7.71-7.69 (m, 4H, Ar*H*), 7.11-6.97 (m, 10H, Ar*H*), 6.89-6.83 (m, 4H, Ar*H*), 6.58-6.49 (m, 4H, Ar*H*), 3.99-3.93 (m, 4H, NC*H*₂), 3.90-3.85 (m, 4H, OC*H*₂), 2.17-2.11 (m, 4H, CH₂C*H*₂CH₂). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 168.4, 157.1, 144.2, 139.6, 136.5, 133.9, 132.5, 132.2, 131.4, 127.6, 126.2, 123.3, 113.5, 65.5, 35.6, 28.3. ESI-MS: *m*/*z* calcd for C₄₈H₃₈N₂NaO₆ [M + Na]⁺ = 761.262, found = 761.10. HR-ESI-MS: *m*/*z* calcd for C₄₈H₃₈N₂NaO₆ [M + Na]⁺ = 761.2620.





Fig. S12. ¹H NMR spectrum (300 MHz, CDCl₃, 298 K) of compound 3.



Fig. S13. ¹³C NMR spectrum (75 MHz, CDCl₃, 298 K) of compound 3.



Fig. S14. Electrospray ionization mass spectrum (CH₃CN) of compound 3.

To a solution of **3** (4.83 g, 6.5 mmol) in EtOH (200 mL) was added hydrazine monohydrate (20 mL) and the mixture was then refluxed for 12 h under N₂ atmosphere. The solvent was removed under vacuum. The residue was dissolved in water (60 mL) and the resulting mixture was extracted with DCM (100 mL × 2). The combined extracts were washed with brine, the organic layer was dried with anhydrous MgSO₄, and concentrated under reduced pressure to afford compound **4** as a light yellow oil (2.58 g, 5.4 mmol). Yield: 83 %. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.04-6.95 (m, 10H, Ar*H*), 6.82 (d, *J* = 8.7 Hz, 4H, Ar*H*), 6.54 (d, *J* = 8.7 Hz, 4H, Ar*H*), 3.88 (t, *J* = 6.0 Hz, 4H, OC*H*₂), 2.80 (t, *J* = 6.6 Hz, 4H, NC*H*₂), 1.84-1.76 (m, 4H, CH₂C*H*₂CH₂), 1.22 (br, 4H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 157.6, 144.3, 139.6, 136.4, 132.6, 131.4, 127.7, 126.2, 113.5, 65.6, 39.3, 33.1. ESI-MS: *m*/*z* calcd for C₃₄H₃₈N₃O₂ [M + H + CH₃CN]⁺ = 520.30, found = 520.70. HR-ESI-MS: *m*/*z* calcd for C₃₂H₃₅N₂O₂ [M + H]⁺ = 479.2693, found =479.2696.





Fig. S15. ¹H NMR spectrum (300 MHz, CDCl₃, 298 K) of compound 2.



Fig. S16. ¹³C NMR spectrum (75 MHz, CDCl₃, 298 K) of compound 2.



Fig. S17. Electrospray ionization mass spectrum (CH₃CN) of compound 2.

Imidazolide **M** (3.60 g, 11.9 mmol) and **2** (2.58 g, 5.4 mmol) were dissolved in dry CHCl₃ (100 mL) and this solution was stirred for 12 h under nitrogen at room temperature. To the reaction mixture CHCl₃ (20 mL) was added and the organic layer was washed with 1 M HCl (50 mL), saturated

NaHCO₃ (50 mL), brine (50 mL), dried with anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (CHCl₃ : MeOH = 100 : 1, v/v) to afford compound **1** as a white solid (4.20 g, 4.4 mmol). Yield: 81 %. ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 13.21 (s, 2H, N*H*), 11.97 (s, 2H, N*H*), 10.31 (s, 2H, N*H*), 7.11-6.98 (m, 10H, Ar*H*), 6.93-6.86 (m, 4H, Ar*H*), 6.67-6.60 (m, 4H, Ar*H*), 5.80 (s, 2H, alkene-*H*), 3.99-3.95 (m, 4H, OC*H*₂), 3.48-3.43 (m, 4H, NC*H*₂), 2.32-2.25 (m, 2H, CH=CR-C*H*-R₂), 2.10-2.06 (m, 4H, alkyl-*H*), 1.68-1.52 (m, 8H, alkyl-*H*), 1.33-1.20 (m, 8H, alkyl-*H*), 0.91-0.86 (m, 12H, CH₂C*H*₃). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 173.1, 157.4, 156.8, 155.5, 154.8, 144.3, 139.6, 136.3, 132.5, 131.39, 127.7, 126.2, 113.6, 106.3, 65.4, 45.4, 37.2, 32.9, 29.3, 26.6, 22.5, 13.9, 11.8. ESI-MS: *m*/*z* calcd for C₅₆H₆₉N₈O₆ [M + H]⁺ = 949.53, found = 949.20. HR-ESI-MS: *m*/*z* calcd for C₅₆H₆₇N₈O₆ [M - H]⁺ = 947.5189, found = 947.5189.



Fig. S18. ¹H NMR spectrum (300 MHz, CDCl₃, 298 K) of 1.



Fig. S19. ¹³C NMR spectrum (75 MHz, CDCl₃, 298 K) of 1.





9. References

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