Supporting Information

Cooperative catalysis of Cu/2,2,6,6-tetramethyl-1-piperidine-*N*-oxyl nanocatalysts supported by ultraviolet light-responsive polyimides

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1. Nomenclature and Abbreviations

Table S1. Nomenclature and abbreviations

Abbreviation	**Name/description**
NMR	nuclear magnetic resonance
TEM	transmission electron microscopy
FT-IR	Fourier-transform infrared spectroscopy
DLS	dynamic light scattering
DMF	*N*,*N*-dimethylformamide
THF	tetrahydrofuran
GPC	gel permeation chromatography
UV-vis	ultraviolet-visible
M_n	number average molecular weight
M_w	weight average molecular weight
PDI	polydispersity index
CuAAC	copper-catalyzed azide-alkyne cycloaddition
XRD	X-ray diffraction
SAXS	small angle x-ray scattering

2. Experimental Section

2.1. Materials

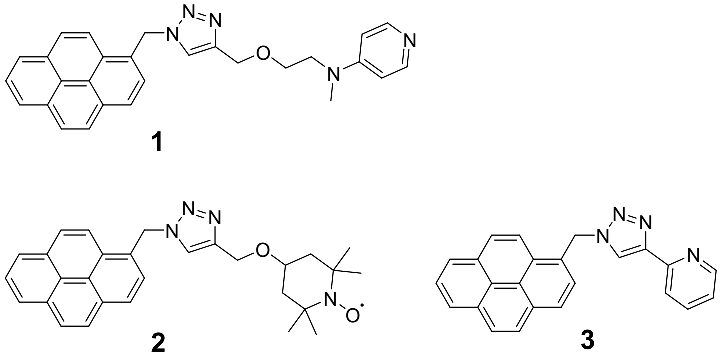
Poly(propylene glycol) bis(2-aminopropyl ether) (M_n ~ 230, ~ 400, and ~ 2000), 1,4,5,8-naphthalenetetracarboxylic dianhydride (96 %), 4,4-azodianiline (≥ 98 %), $CuSO_4 \cdot 5H_2O$ (99 %), Triton X-100 (AR), and benzyl alcohol (≥ 99 %) were purchased from Shanghai Macklin Biochemical Co., Ltd. Unless otherwise stated, all chemicals were used as received.

2.2. Characterization

Gel permeation chromatography (GPC) measurements were conducted on an Agilent PL-GPC50 at 40 °C by using tetrahydrofuran (THF) as the eluent. Proton nuclear magnetic resonance (^1H NMR) measurements were carried out on a Varian Inova 400 instrument at 25 °C, and residual solvent peaks are chosen as internal standards. Ultraviolet visible (UV-vis) measurements were performed on a MAPADA UV-1600 instrument (Shanghai MAPADA Instruments Co., Ltd) at 25 °C. UV-vis spectra were corrected against appropriate background spectra. Transmission electron microscope (TEM) images were taken on a Tecnai G2 Spirit TWIN microscope (FEI company, operating at 120 kV). Samples were prepared by dropping dispersed solutions of substrates onto carbon-coated copper grids, and solvent was allowed to dry under ambient conditions before observation. At least five different positions were studied for each sample. Dynamic light scattering (DLS) measurements at 25 °C were carried out on a Zetasizer Nano ZS (Malvern Instruments Ltd) equipped with a 632.8 nm He-Ne laser. The measurement angle was kept at 173°. X-ray diffraction (XRD) measurements were conducted on a Bruker D8 Advance equipped with Cu Kα radiation (λ= 0.154056 nm, 2θ from 5^{o} to 115^{o}). Small angle X-ray scattering (SAXS) measurements were carried out on a Xenocs Xeuss 2.0 equipped with Cu Kα radiation (λ= 0.154189 nm). Nanoparticles were collected by centrifugation, dried under reduced pressure at room temperature, and used for both XRD and SAXS measurements.

2.3. Synthesis of 1, 2, and 3

Scheme S1. Chemical structures of **1**, **2**, and **3**.



The synthesis and characterization of **1**, **2**, and **3** were reported in our previous work.[1]

2.4. Synthesis of P1, P2, P3, P4 and P5

Azobenzene-containing polymers (**P1**, **P2**, **P3**, **P4**, and **P5**) were synthesized as follows. Firstly, 4,4-azodianiline, poly(propylene glycol) bis(2-aminopropyl ether), and 1,4,5,8-naphthalenetetracarboxylic dianhydride were mixed with THF (Table S2). The resulting mixtures were stirred at room temperature for 12 hours. After which, the solvent was removed under reduced pressure. And the residues were kept at 190 ^{o}C under vacuum for three hours to obtain dark brown polymers. The synthesis and characterization of **P6** were reported in our previous work.[1]

Scheme S2. Synthesis of **P1**, **P2**, **P3**, **P4** and **P5**

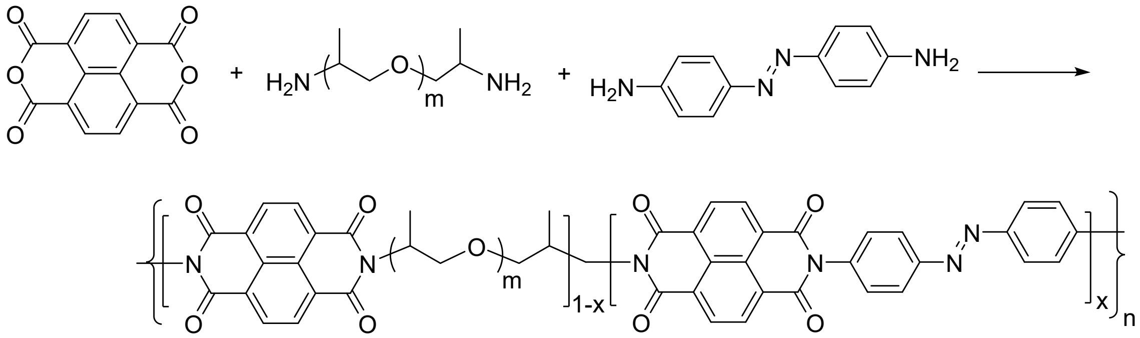


Table S2. Feed amount ratio of **P1**, **P2**, **P3**, **P4** and **P5**.

Polymer	1,4,5,8-Naphthalenetetracarboxylic dianhydride / mg	Poly(propylene glycol) bis(2-aminopropyl ether)		4,4'-Azodianiline / mg	THF / mL	Yield / %
		M_n	Feed amount / mg			
P1	54	~2000	340	6	2.5	74
P2	54	~2000	360	4	2.5	77
P3	54	~2000	380	2	2.5	79
P4	107	~400	144	8	2.5	81
P5	107	~230	83	8	2.5	78

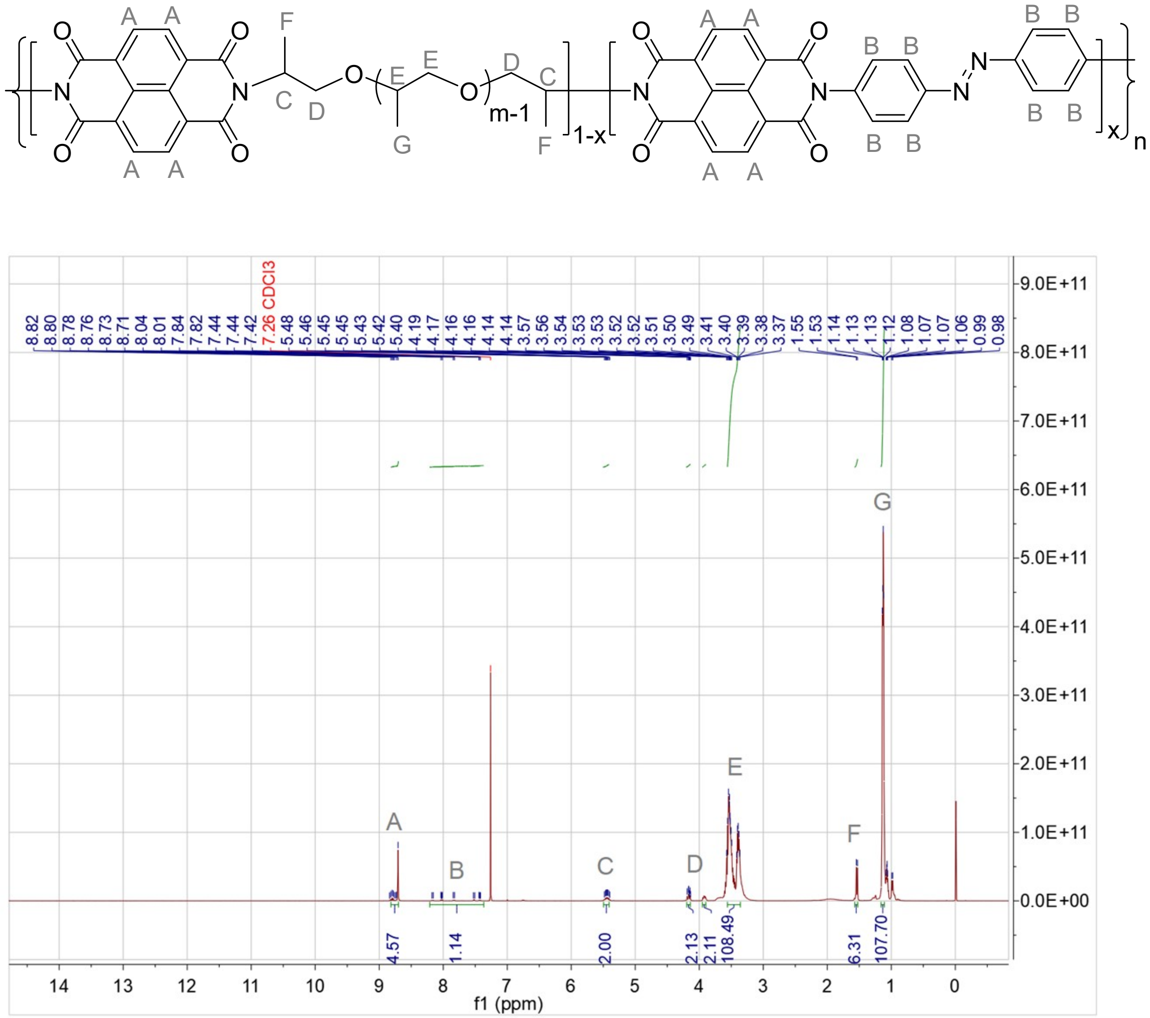


Figure S1. ^{1}H NMR spectrum in $CDCl_3$ of **P1**.

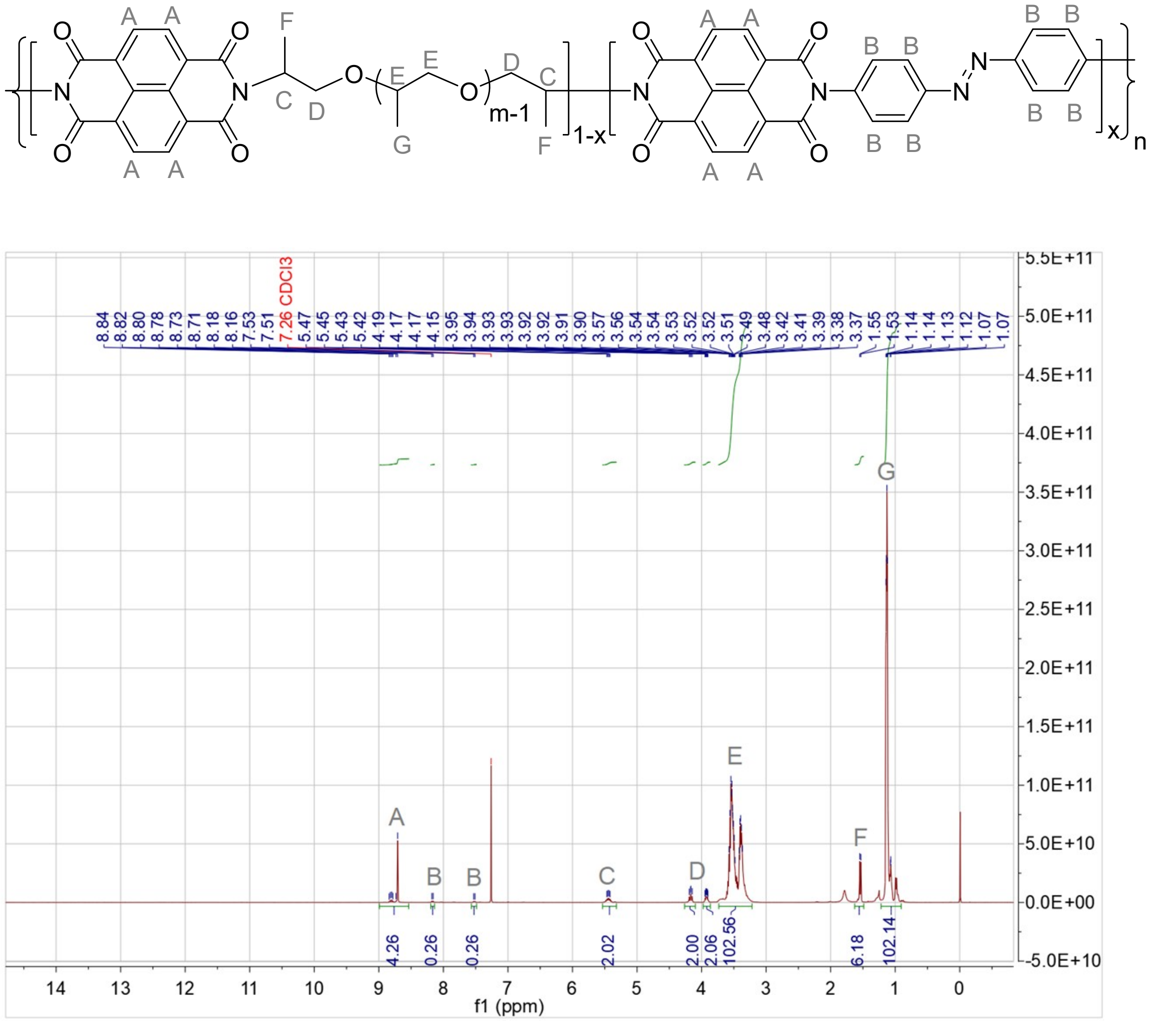


Figure S2. ^{1}H NMR spectrum in $CDCl_3$ of **P2**.

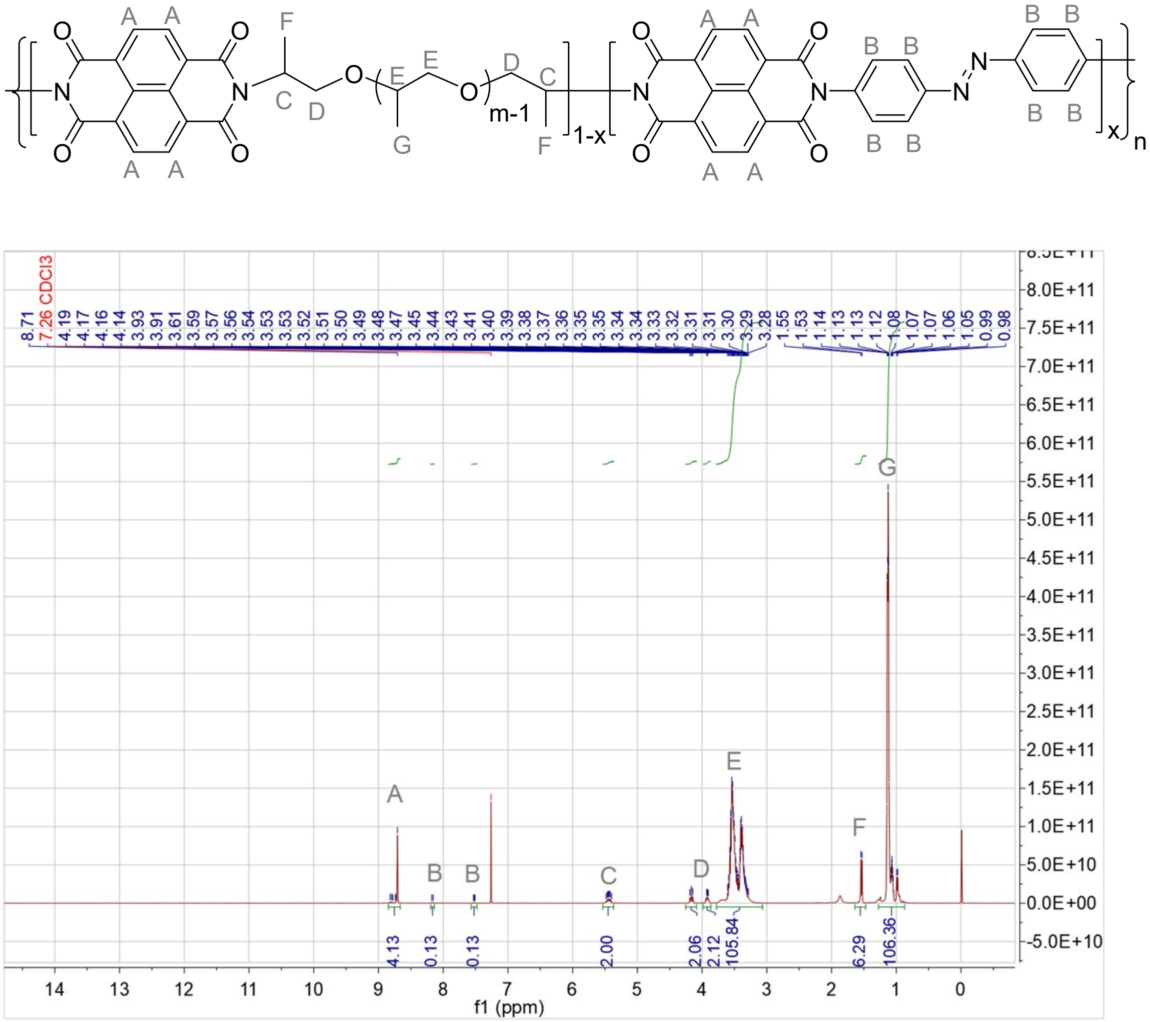


Figure S3. ^{1}H NMR spectrum in $CDCl_3$ of **P3**.

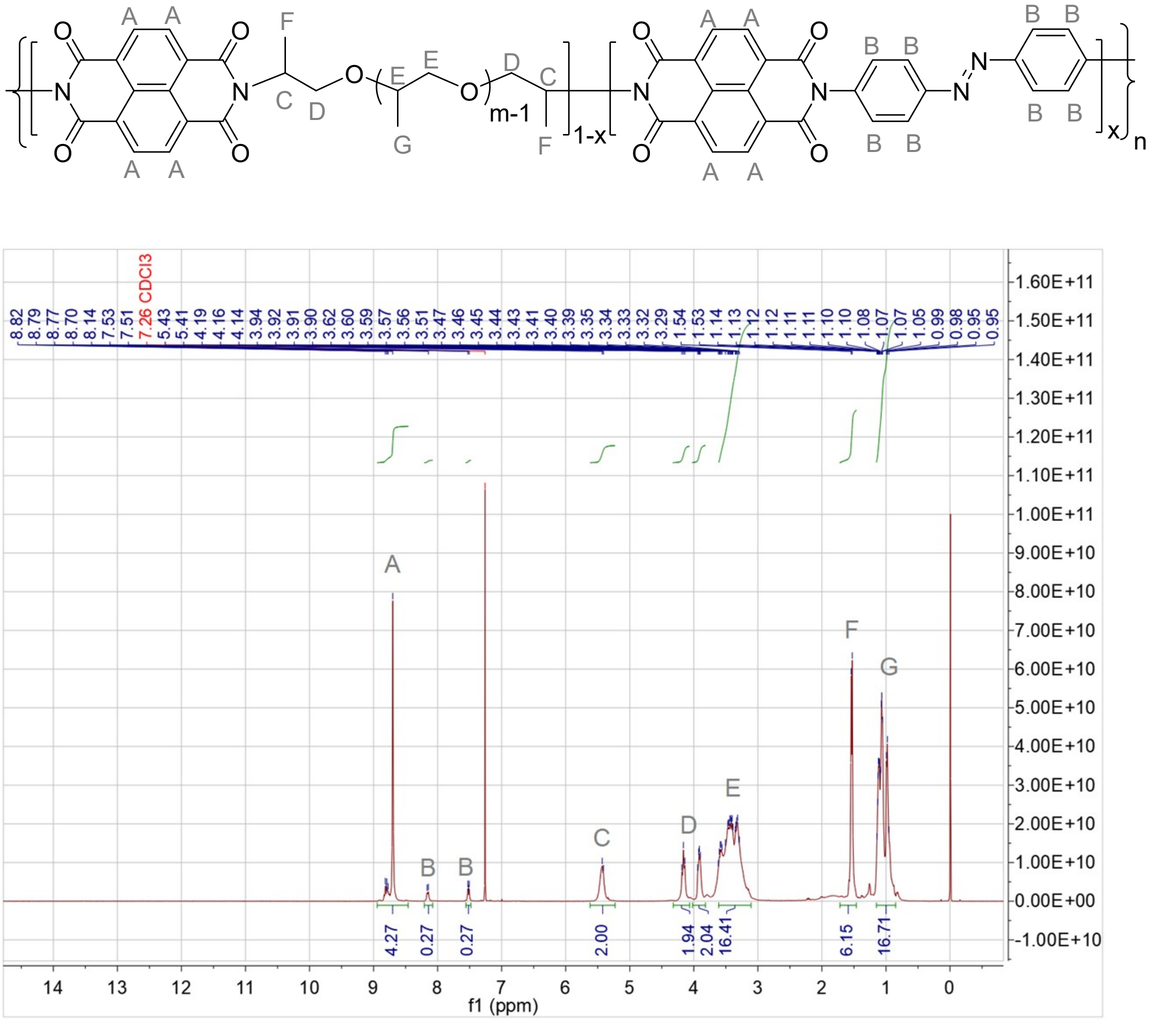


Figure S4. ^{1}H NMR spectrum in $CDCl_3$ of **P4**.

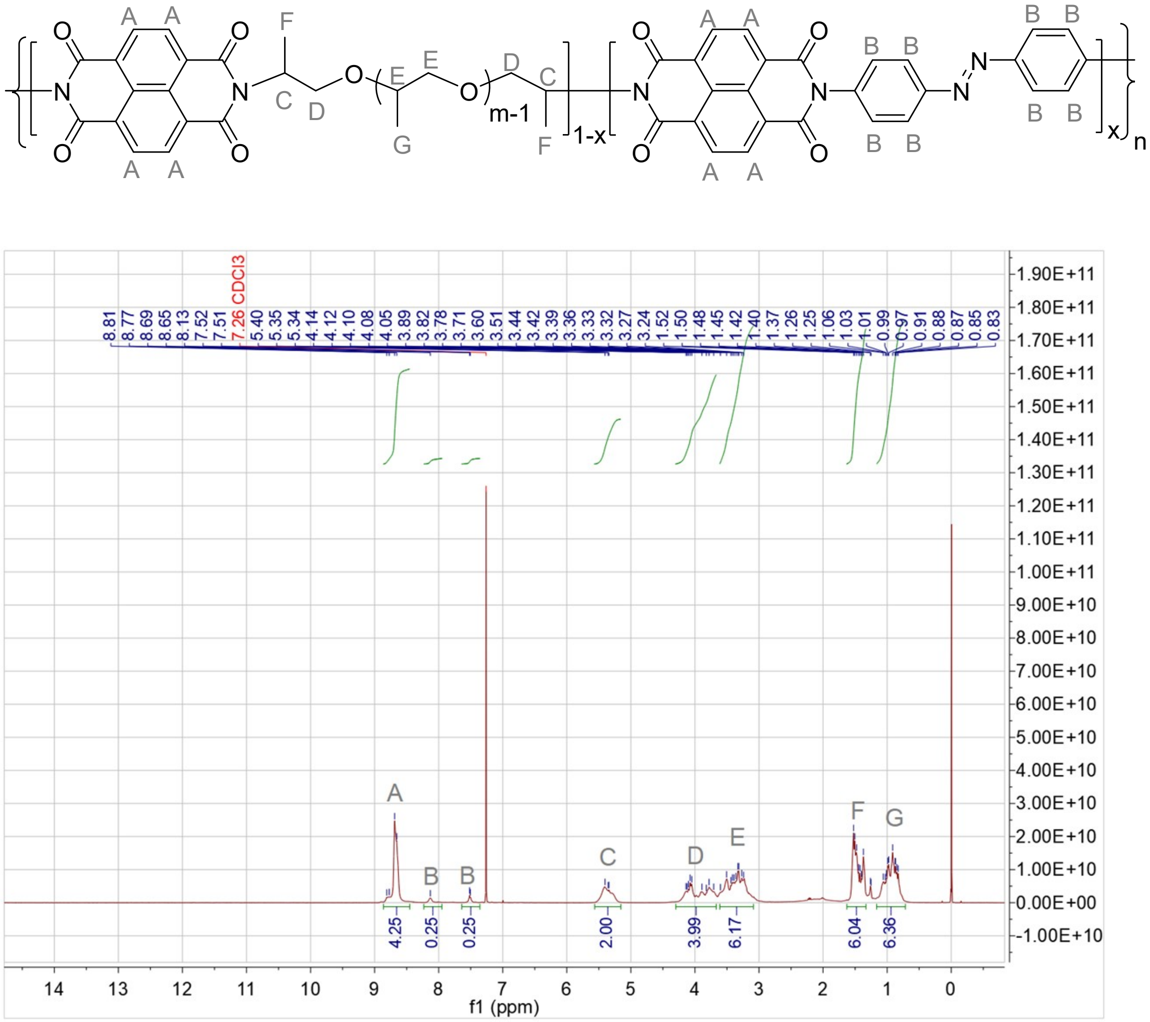
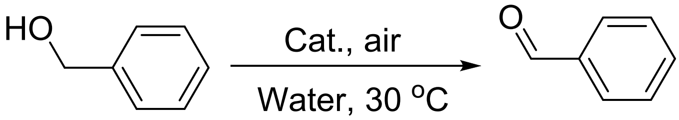


Figure S5. ^{1}H NMR spectrum in CDCl$_3$ of **P5**.

2.5. General procedure for preparation of nanoparticle catalysts and aerobic oxidation of BnOH



Scheme S3. Oxidation of BnOH to benzaldehyde under air in water.

To 9 mL of an aqueous solution containing both Triton X-100 (100 μmol) and $CuSO_4·5H_2O$ (25 μmol), 2 mL of a DMF solution containing catalytic components were quickly added under stirring (700 r/min) at room temperature to give an emulsion. After stirring for 30 min in open air, a drop of the resulting emulsion was taken for further characterization. To the emulsion, 1 mL of H_2O and BnOH (5 mmol) were added. The resulting mixture was stirred at 30 ^oC for 12 hours in open air. After that, the mixture was extracted with petroleum ether (PE). The conversion and selectivity for benzaldehyde were determined by ^1H NMR measurements. Turnover frequency (TOF) was determined according to the following equation: TOF = $(n_{con}/n_{Cu})/t$, where n_{Cu} is the amount of copper ions added; n_{con} is the amount of benzyl alcohol consumed; t is the reaction time.

3. GPC Data

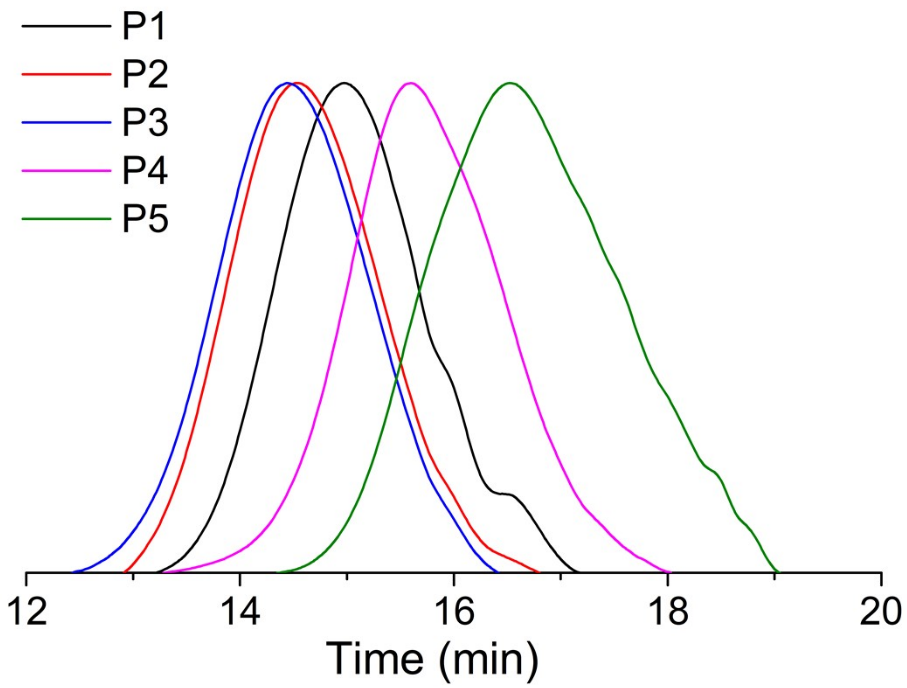


Figure S6. GPC traces of **P1**, **P2**, **P3**, **P4**, and **P5**.

Table S3. GPC characterization of **P1**, **P2**, **P3**, **P4**, and **P5**.

Polymer	$M_n{}^a$	$M_w{}^a$	PDI^a
P1	14000	26400	1.88
P2	24200	43900	1.81
P3	28500	52500	1.84
P4	6200	12600	2.10
P5	1800	4500	2.50

[a] Determined by GPC using polystyrene as calibration standard.

4. UV-vis Spectra

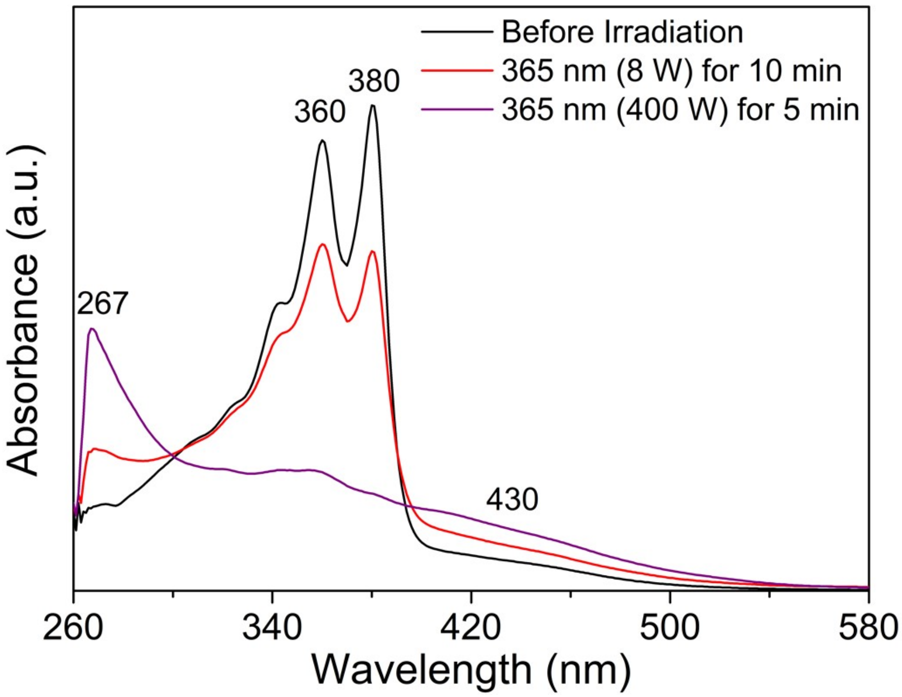


Figure S7. UV-vis spectra in DMF of **P1** before and after irradiation.

5. TEM Images

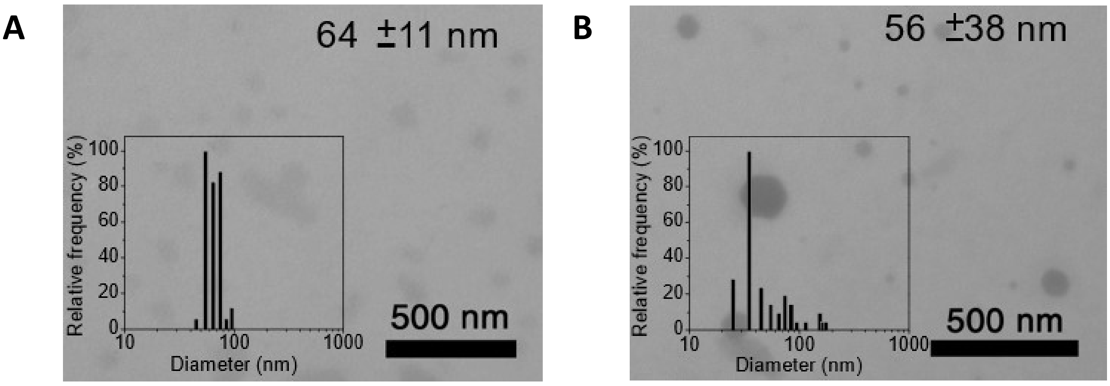


Figure S8. Typical TEM images of nanoparticle catalysts prepared by using **1**/**2**/**3**/**P1** (10/5/5/5 mol%, effective constituent ratio relative to BnOH) (A) without and (B) with UV light (365 nm, 400 W, 5 min) irradiation.

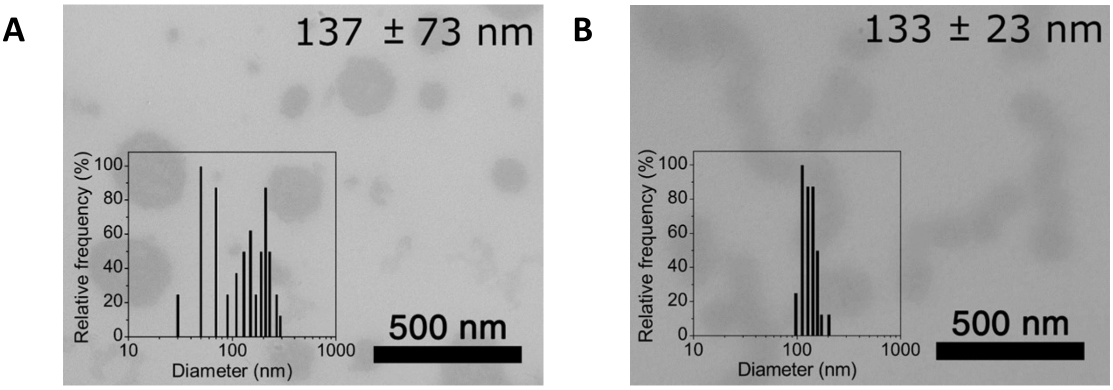


Figure S9. Typical TEM images of nanoparticle catalysts prepared by using **1**/**2**/**3**/**P2** (10/5/5/5 mol%, effective constituent ratio relative to BnOH) (A) without and (B) with UV light (365 nm, 400 W, 5 min) irradiation.

6. DLS Data

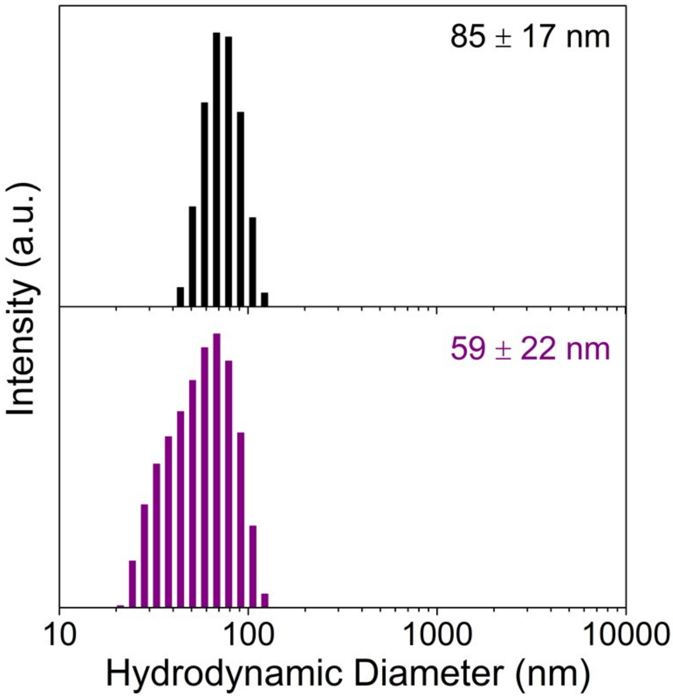


Figure S10. Size distributions of nanoparticles prepared by using **1**/**2**/**3**/**P1** (10/5/5/5 mol%) without (black bars) and with UV light (365 nm, 400 W, 5 min) irradiation (purple bars).

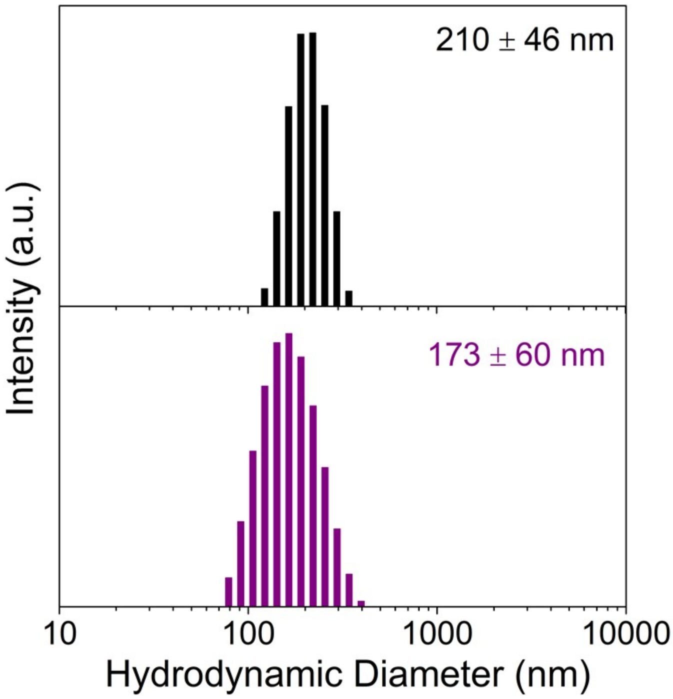


Figure S11. Size distributions of nanoparticles prepared by using **1**/**2**/**3**/**P2** (10/5/5/5 mol%) without (black bars) and with UV light (365 nm, 400 W, 5 min) irradiation (purple bars).

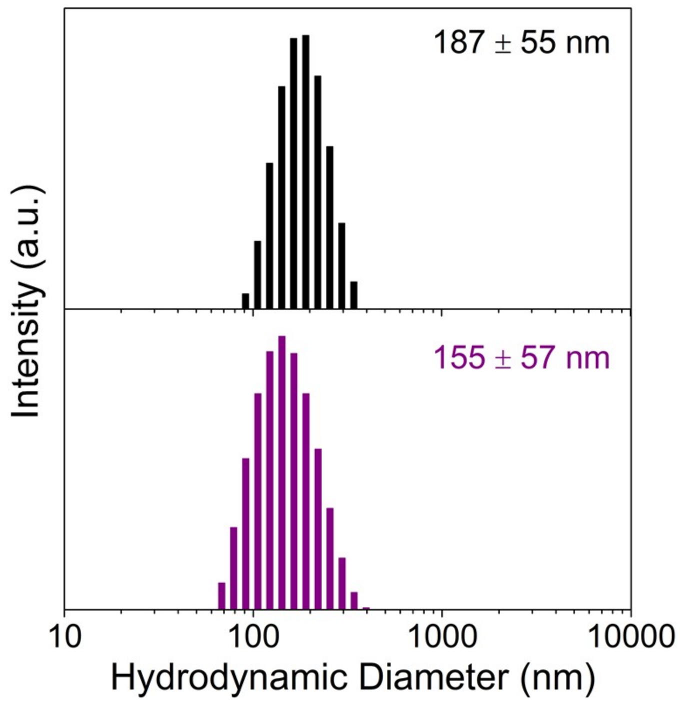


Figure S12. Size distributions of nanoparticles prepared by using **1**/**2**/**3**/**P3** (10/5/5/5 mol%) without (black bars) and with UV light (365 nm, 400 W, 5 min) irradiation (purple bars).

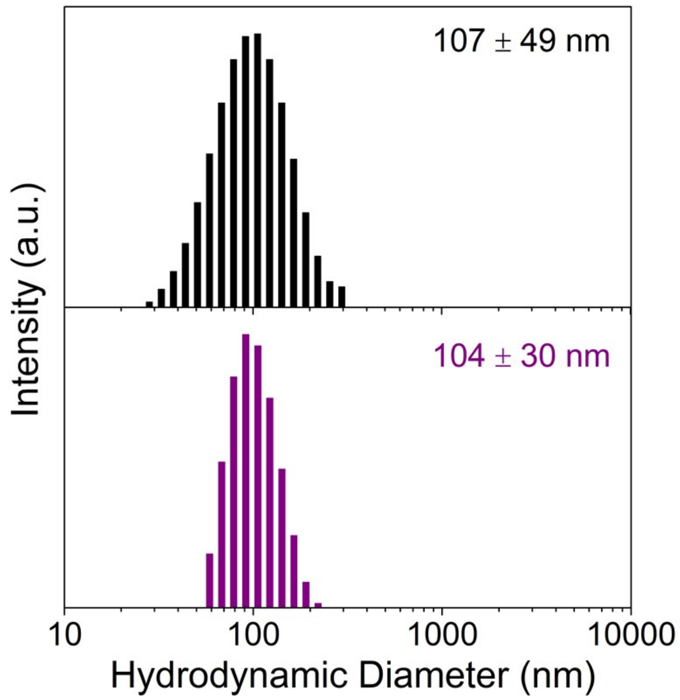


Figure S13. Size distributions of nanoparticles prepared by using **1**/**2**/**3**/**P4** (10/5/5/5 mol%) without (black bars) and with UV light (365 nm, 400 W, 5 min) irradiation (purple bars).

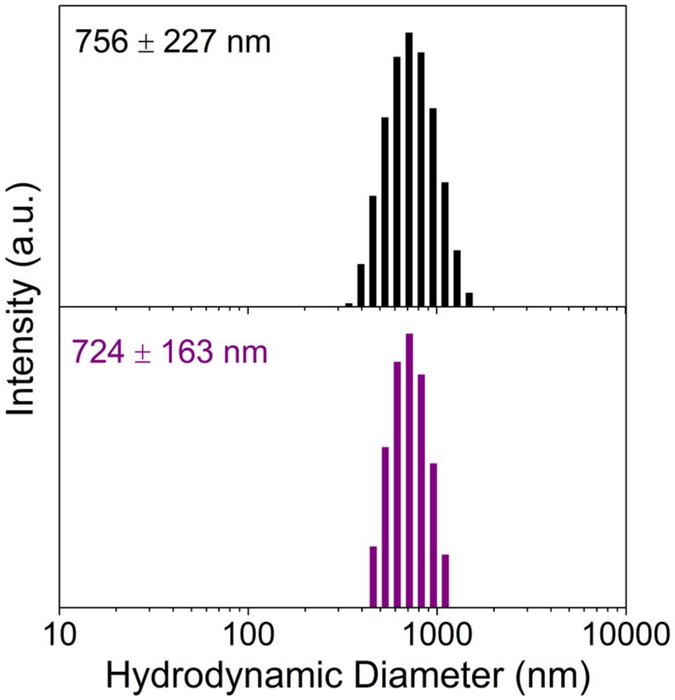


Figure S14. Size distributions of nanoparticles prepared by using **1**/**2**/**3**/**P5** (10/5/5/5 mol%) without (black bars) and with UV light (365 nm, 400 W, 5 min) irradiation (purple bars).

7. SAXS Data

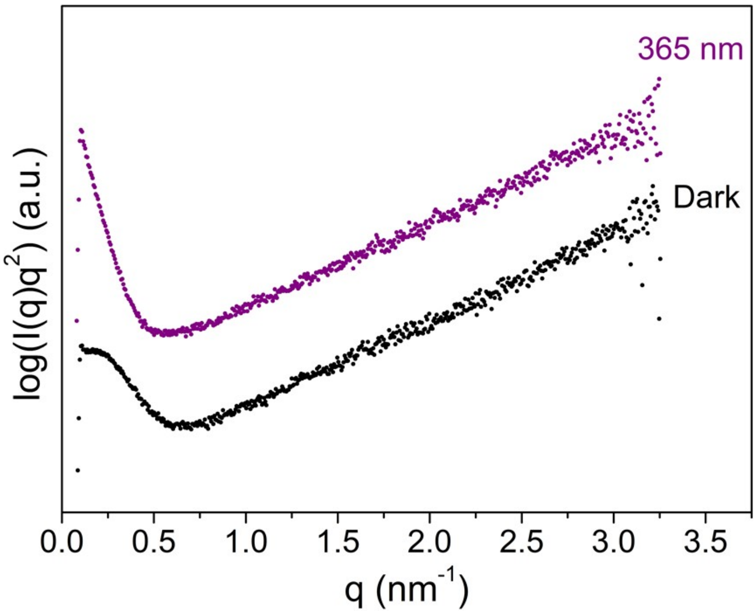


Figure S15. SAXS of nanoparticles prepared by using **1**/**2**/**3**/**P1** (10/5/5/5 mol%) without (black) and with UV light (365 nm, 400 W, 5 min) irradiation (purple).

8. TOF Comparison

Table S4. TOF comparison of this work with reported catalysts in water using air as the oxidant.

Catalyst	Temp.	TOF/h^{-1}	Ref
$CuFe_2O_4$ nanoparticle/TEMPO	100 °C	0.53	[2]
MCM-41-bpy-CuI/TEMPO/$NH_3 \cdot H_2O$[a]	30 °C	0.28	[3]
CuI-Y Zeolite/TEMPO	r. t.	0.02	[4]
Polystyrene-supported Cu/TEMPO	30 °C	0.48	[5]
Pyrene-containing polymer-supported Cu/TEMPO	30 °C	0.67	[6]
Polyimide-supported Cu/TEMPO	30 °C	1.18	[1]
Azobenzene-containing polyimide-supported Cu/TEMPO	30 °C	2.11	This work

[a] 4-Methoxybenzyl alcohol as the substrate and acetonitrile/H_2O (2/1) as the solvent.

9. XRD Data

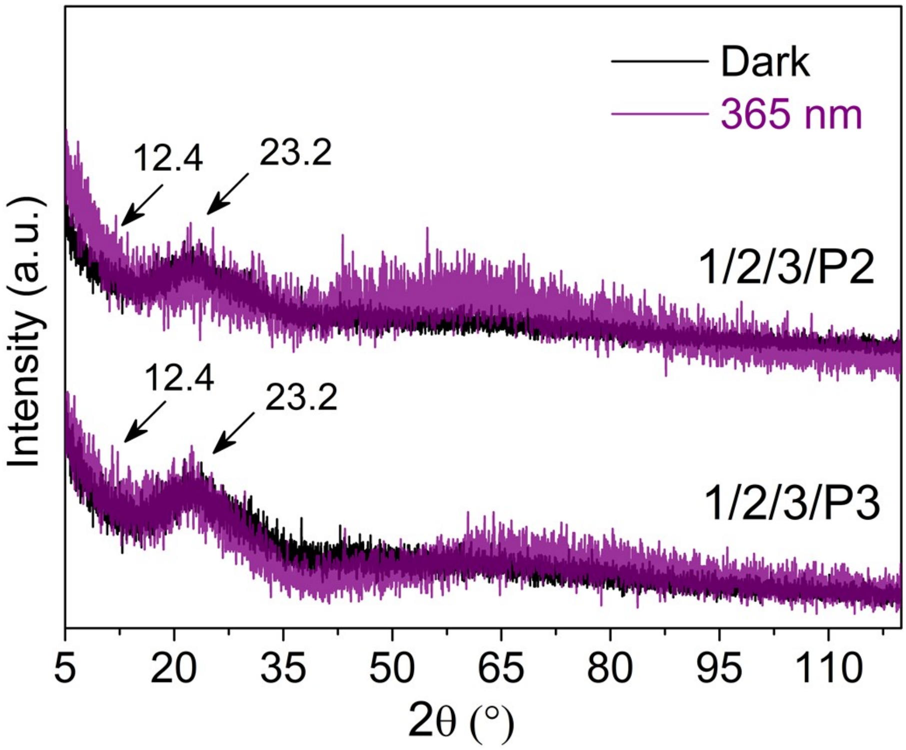


Figure S16. XRD patterns of nanocatalysts prepared by using **1**/**2**/**3**/**P2** (10/5/5/5 mol%) and **1**/**2**/**3**/**P3** (10/5/5/5 mol%) without or with UV light (365 nm, 400 W, 5 min) irradiation.

10. Recycling

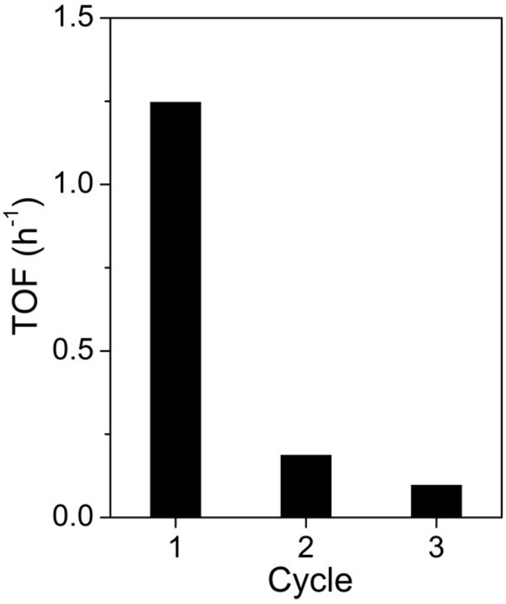


Figure S17. Recycling of the nanocatalyst prepared by using **1**/**2**/**3**/**P1** (10/5/5/5 mol%) with UV light (365 nm, 400 W, 5 min) irradiation.

11. References

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