

Electronic supplementary information for

8-Hydroxyquinoline and its derivatives functionalized $\text{Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y$ alloyed NCs: optical and photophysical properties

1. Materials and methods

1.1 Materials

Cadmium oxide (CdO, 99.99%), zinc acetate (99.9%, powder), selenium (99.9%, powder), sulfur (99.9%, powder), trioctylphosphine (TOP, 90%), oleic acid (OA, 90%) and 1-octadecene (ODE, 90%) were used as purchased from Aldrich. ZnCl_2 (99%) and $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (99%) were obtained from Shanghai Reagent Company. Other chemicals were of analytical grade without purification.

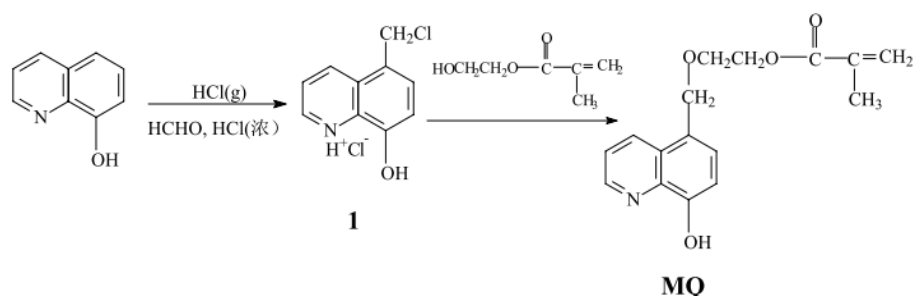
1.2 Synthesis of $\text{Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y$ NCs¹

As a typical synthetic procedure, 0.4 mmol of CdO, 4 mmol of zinc acetate, 17.6 mmol of oleic acid, and 20 mL of 1-octadecene were placed in a 100 mL round flask. The mixture was heated to 150 °C to degass, filled with N_2 gas, and further heated to 310 °C to form a clear solution of $\text{Cd}(\text{OA})_2$ and $\text{Zn}(\text{OA})_2$. At this temperature, 0.4 mmol of Se powder and 4 mmol of S powder both dissolved in 3 mL of TOP were quickly injected into the reaction flask. After the injection, the temperature of the reaction flask was set to 300 °C for promoting the growth of NCs, and it was then cooled to room temperature to stop the growth.

1.3 Synthesis of 5-(2-methacryloyloxyethyl)-8-quinolinol (MQ)

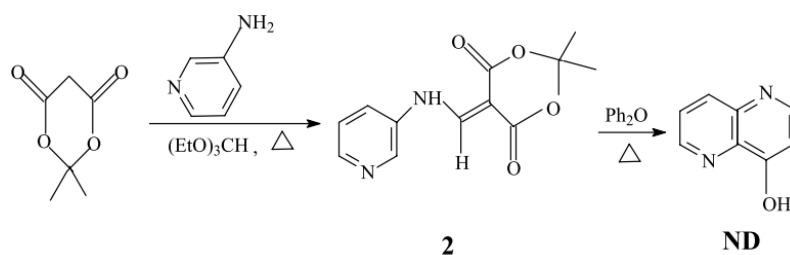
MQ was synthesized according to a previous procedure.² ^1H NMR (500MHz, CDCl_3): 8.78

(1H, Ph-H), 8.50 (1H, Ph-H), 7.46 (1H, Ph-H), 7.40 (1H, Ph-H), 7.08 (1H, Ph-H), 6.03(1H, =CH₂), 5.52 (1H, =CH₂), 4.87 (2H, OCH₂OPh), 4.27, 3.69 (4H, OCH₂OO), 1.88 (3H, OCH₃).



1.4 Synthesis of 4-hydroxy-1,5-naphthyridine (ND)

ND was synthesized according to a previous report.³ ¹H NMR (500 MHz, CD₃OD): δ 8.74 (1H, ND-H), 8.07 (1H, ND-H), 8.04 (1H, ND-H), 7.72 (1H, ND-H), 6.51 (1H, ND-H).



1.5 Synthesis of functionalized Cd_{1-x}Zn_xSe_{1-y}S_y alloyed NCs

Different HQ derivatives functionalized NCs were prepared via ligand exchange process. As a typical synthetic procedure, HQ-NCs were prepared by the addition of HQ to 5 mL chloroform containing 0.1g Cd_{1-x}Zn_xSe_{1-y}S_y NCs, followed by stirring for 24 h at room temperature. The ratio of adsorbed HQ to NCs was controlled by varying the amount of added HQ as the recipes showed in Table S1. HQ-NCs were purified by adding an excess amount of acetone (3 times) to remove uncoordinated HQ molecules. MQ and ND functionalized NCs, defined as MQ-NCs and ND-NCs, were prepared by same method.

1.6 Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Magna 560 FTIR spectrometer.

UV–vis absorption spectra were recorded on a Shimadzu UV-2550 UV–vis spectrometer in the range 200–800 nm. The PL properties were measured on a Cary Eclipse fluorescence spectrometer. $^1\text{H-NMR}$ spectra (in CDCl_3) were recorded on a DRX-400 MHz (Bruker) spectrometer with TMS as an internal standard. X-ray powder diffraction (XRD) analysis was measured using a Rigaku D/max-IIB with $\text{CuK}\alpha$ radiation ($\lambda = 1.5 \text{ \AA}$). Transmission electron microscopy (TEM) was recorded on a JEM-2100 microscope. Luminescence lifetime were measured with a Lecroy Wave Runner 6100 digital oscilloscope (1 GHz) using a 355 nm laser radiation (pulse width = 4 ns) as the excitation source (ContinuumSunliteOPO). Cyclic voltammetry (CV) was performed on an electrochemical workstation CHI-660D. For electrochemical studies, purified NCs were dried in vacuum, and 0.5 mg was dissolved in 5mL of high-purity chloroform containing 0.1 M tetra-n-butylammoniumhexafluorophosphate (Aldrich) as a supporting electrolyte. Experiments were carried out in a one compartment electrochemical cell using a platinum disk electrode (0.02 cm^2) as working electrode, a Ag/Ag^+ reference electrode and platinum foil as a counter electrode. The reference potential was estimated against the standard hydrogen electrode (SHE), taking the formal potential of the ferrocene couple (used as an internal reference) as 0.64 V vs SHE. The solution was purged with Ar for at least 5 min before each experiment. All the CV experiments were carried out in chloroform solutions at room temperature. The fluorescence quantum yields (QYs) of the NCs were determined by comparing their fluorescence intensities with those of Rhodamine B (QY: 0.69) as a reference, both excited at 390nm. The absorbances of both solutions were between 0.02 and 0.05.

2. Supporting Tables

Table S1 Recipes for synthesis of Q-NCs, MQ-NCs and ND-NCs with different ligand ratios.

Samples	m_{NCs}/g	$m_{\text{ligand}}/\text{g}$
Q-NCs (1:50)	0.1	0.002
Q-NCs (1:20)	0.1	0.005
Q-NCs (1:10)	0.1	0.01
Q-NCs (1:7.5)	0.1	0.013
Q-NCs (1:5)	0.1	0.02
Q-NCs (1:2)	0.1	0.05
Q-NCs (1:1)	0.1	0.1
MQ-NCs (1:10)	0.1	0.01
MQ-NCs (1:5)	0.1	0.05
MQ-NCs (1:1)	0.1	0.1
ND-NCs (1:15)	0.1	0.007
ND-NCs (1:10)	0.1	0.01
ND-NCs (1:5)	0.1	0.05
ND-NCs (1:1)	0.1	0.1

Table S2 Fluorescence decay and QY data of different functionalized NCs.

Samples	τ_1 (ns) ^a	b_1	τ_2 (ns)	b_2	$\langle\tau\rangle_{505(455)}^b$	τ_1 (ns)	b_1	τ_2 (ns)	b_2	$\langle\tau\rangle_{575}$	QY ^d
	505nm ^c	%	505(455)nm ^c	%	(ns)	575nm	%	575nm	%	(ns)	%
NCs	—	—	—	—	—	9.72	59.66	24.06	40.34	15.50	75
Q-NCs (1:10)	8.83	41.03	18.75	58.97	14.68	10.41	55.78	23.79	44.22	16.33	54
Q-NCs (1:5)	9.33	57.06	19.64	42.94	13.76	8.35	51.82	21.53	48.18	14.70	37
MQ-NCs (1:10)	—	—	—	—	—	9.40	44.00	22.05	56.00	16.48	59
MQ-NCs (1:5)	—	—	—	—	—	14.95	55.64	48.27	44.36	29.73	41
ND-NCs (1:10)	3.35	34.69	18.42	65.31	13.19	13.64	67.08	69.03	32.92	31.87	57
ND-NCs (1:5)	2.58	31.44	16.81	68.56	12.42	2.00	34.27	18.24	65.73	12.67	29

^aThe decay time of the solid-state samples was obtained from the decay curves, which simulated by using the multiexponential

model $I(t) = \sum_{i=1}^n \alpha_i \exp(-t/\tau_i)$. Above all samples show the biexponential fluorescence decay. ^b Average fluorescence lifetime

$\langle\tau\rangle = (b_1\tau_1 + b_2\tau_2)$. ^cThe decay of the emissions is registered at $\lambda_{em} = 505$ nm and 575 nm for all samples except for ND-NCs at

$\lambda_{em} = 455$ nm and 575 nm. ^d The quantum yield (QY) was measured following the published procedure reported by Pradhan et al.⁴

For the PL QY determination, the excitation wavelength was chosen to be 390 nm.

3. Supporting Figures

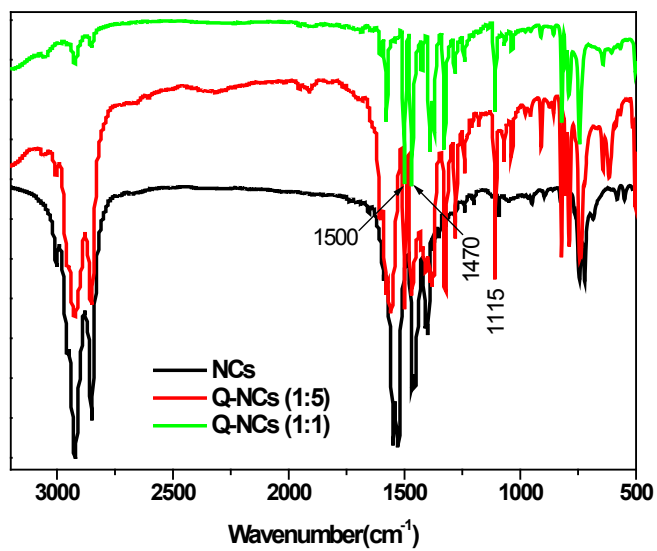


Fig.S1 FTIR spectra of NCs and Q-NCs.

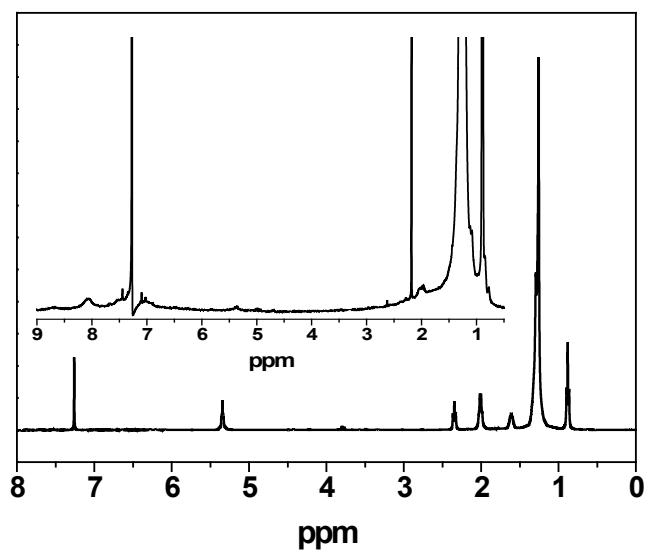


Fig.S2 ^1H NMR spectra of NCs and Q-NCs (1:1) (Inset).

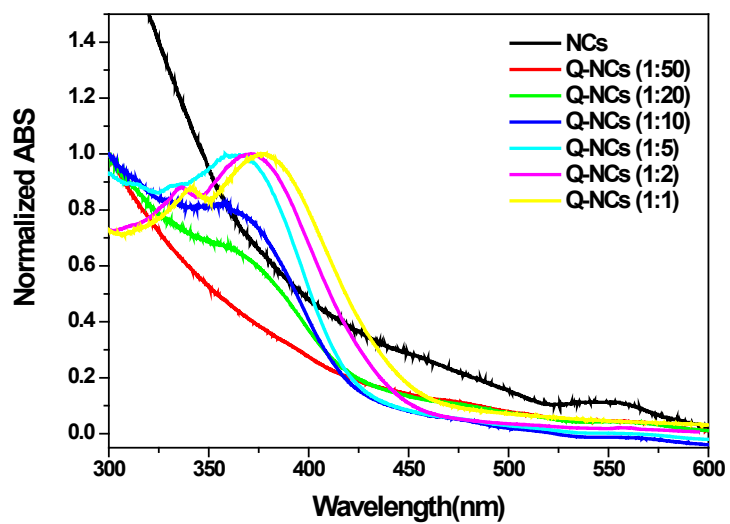


Fig.S3 UV-vis absorption spectra of NCs and Q-NCs.

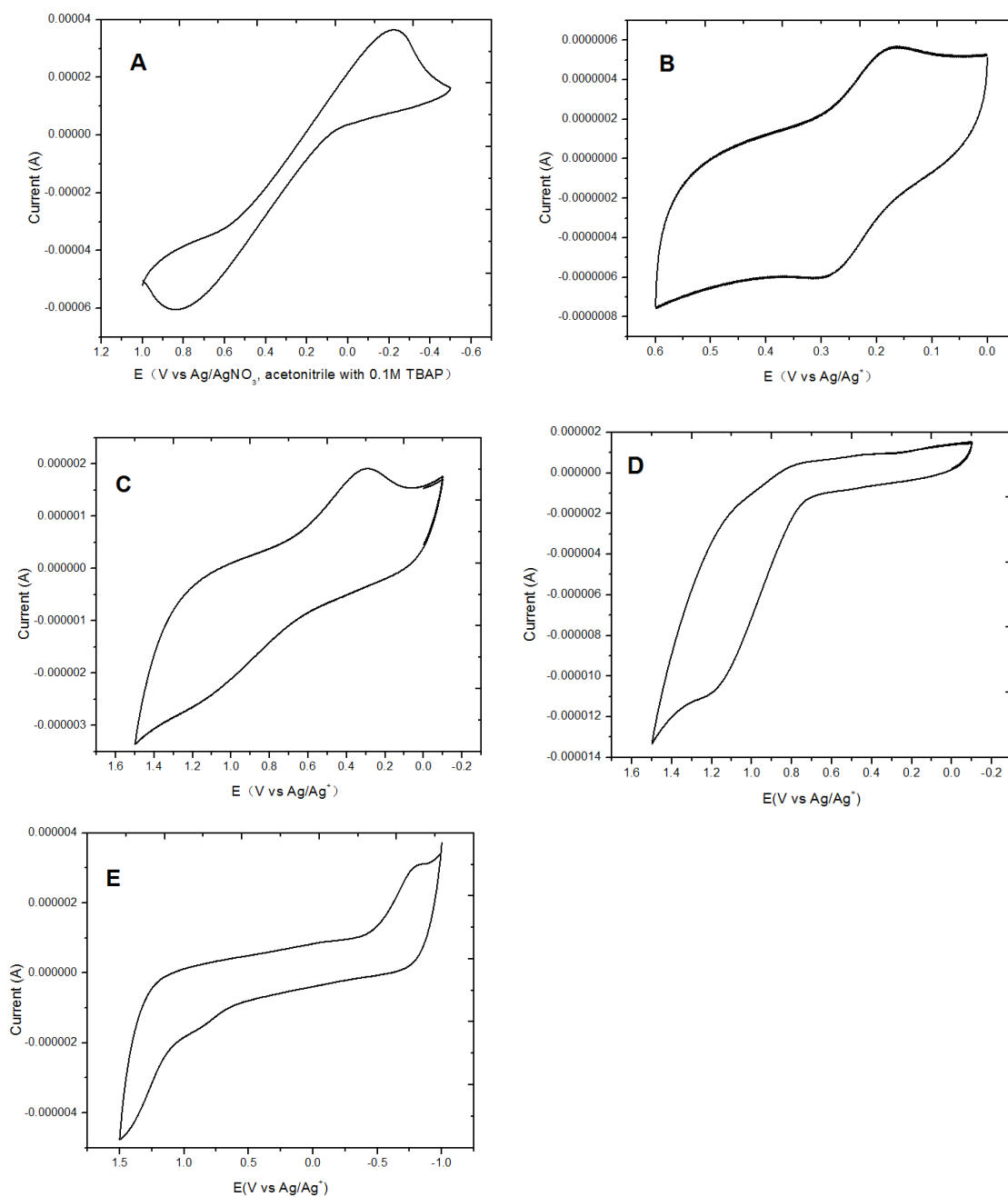


Fig.S4 Cyclic voltammograms of (A) ferrocene, (B) NCs, (C) Zn²⁺-HQ complex, (D) Zn²⁺-MQ complex and (E) Zn²⁺-ND complex in 0.1 M TBAPF6 solutions of chloroform at a scan rate of 50 mV s⁻¹.

References

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