Supplementary information for

Optically Patternable Intensely Luminescent All-Inorganic Nanocrystals

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Experimental Procedures

1. Materials

The following chemicals were used as received: Cadmium oxide (CdO, 99.99%, Aladdin), zinc oxide (ZnO, 99.999%, Aladdin), $Cd(OAc)_2{\cdot}2H_2O$ (99.99%, Aldrich), $Zn(OAc)_2{\cdot}2H_2O$ (99.99%, Aldrich), $Cd(NO3)_2{\cdot}4H_2O$ (99.99%, Aladdin), $Zn(NO3)_2{\cdot}6H_2O$ (99.99%, Aladdin), $In(NO3)_3{\cdot}xH_2O$ (99.99%, Alfa Aesar), $Pb(NO3)_2$ (99.99%, Aladdin), $ZnCl_2$ (99.95%, Alfa Aesar), selenium shots (99.999%,Aladdin), S pillows (99.999%, Alfa Aesar), ammonium thiocyanate (99.99%, Aldrich), trioctylphosphine (TOP, Strem, 97%), trioctylphosphine oxide (TOPO, 90%, Aladdin), tributylphosphine (TBP, 95%, Aladdin), triphenylphosphine (TPP, 99%, Aladdin), oleic acid (OA, 90%, Alfa Aesar), myristic acid (MA, 99%, Aldrich), n-butylamine (99%, Sinopharm), oleylamine (95%, Strem), n-octanethiol (98%, Aladdin), octadecene (ODE, 90%, Alfa Aesar), mercaptopropionic acid (MPA, 98%, Aladdin), sodium citrate dihydrate (CA, 99%, Aladdin), trans-o-coumaric acid (97%, Aladdin) 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, 98%, Aladdin), nitrosonium tetrafluoroborate ($NOBF_4$, 98%, Alfa Aesar), triethyloxonium tetrafluoroborate (Et_3OBF_4, 1 M in DCM, J&K), N,N-dimethylformamide (DMF, 99.9% anhydrous, Alfa Aesar), N-methyl formamide (99%, Alfa Aesar), ethylene glycol (99.5%, Sinopharm), CdSe/ZnS core-shell NCs (5 mg/mL in octane, Najing Tech).

2. Nanocrystal (NC) synthesis

Synthesis of CdSe NCs.[1] Cadmium oleate ($Cd(OA)_2$) stock solution was prepared by mixing CdO (643 mg, 5 mmol) with 10 mL of oleic acid (OA). After degassing at 150 °C, the flask was heated to 250 °C under dry N_2. The suspension then became a colorless solution, indicating the formation of $Cd(OA)_2$. Then degas at 150 °C again to scavenge the generating water and store it as a waxy solid. For the synthesis of wurtzite CdSe NCs, we mixed $Cd(OA)_2$ stock solution (2.25 mL), TOPO (1.2 g) and ODE (12 mL) , which was degassed at 100 °C under vacuum. The temperature was then increased to 300 °C under N_2. At that point, a mixture containing 4 mL of TOPSe (1.0 M) and 3 mL of oleylamine was swiftly injected into the flask. The reaction was kept for 7 min and then cooled down to room temperature. EtOH was added to precipitate the resulting NCs, which were redissolved in toluene next. The washing process was repeated three times and the purified NCs were finally dissolved in 5 mL of toluene.

Synthesis of CdSe/CdZnSeS/ZnS core-shell NCs.[2] Zinc oleate ($Zn(OA)_2$) stock solution was prepared by mixing 405 mg (5 mmol) ZnO with 10 mL of oleic acid (OA). After heating under vacuum at 120 °C, the flask was refilled with N_2 and the temperature was raised to 240 °C. The suspension then became a light yellow solution, indicating the formation of $Zn(OA)_2$. The heater was removed, and the flask was allowed to cool down to 100 °C. Then, 15 mL of ODE and 25mL of oleylamine were added. The obtained solution was degassed at 120 °C and stored in glovebox. For the formation of core-shell NCs, $Zn(OA)_2$ (0.08 M) and 1-octanethiol (0.09 M) were synchronously injected into the hot CdZnSeS

core mentioned above by a dual-channel syringe pump at a rate of 2.5 mL/h for one hour. The resulting CdZnSeS/ZnS NCs were washed with toluene/EtOH and finally redissolved in toluene.

Synthesis of CdZnS/ZnS core-shell NCs.[3] CdO (1 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (5 mmol), OA (3.5 mL) and ODE (7.5 mL) were mixed in a three-neck flask. After degassing at 100 °C, the mixture was heated to 300 °C under nitrogen gas. 1 mmol of sulfur powder was quckly dissolved in ODE (1.5 mL) at approximately 100 °C and the solution was swiftly injected into the flask as soon as the temperature reached 300 °C. The reaction was kept at 310 °C for 8 minutes. Then, 1.5 mL of TBP containing 4 mmol of sulfur was injected for shell growth. The shell-growth step lasted for 40 minutes. The resulting CdZnS/ZnS NCs were washed with hexane/acetone and finally redissolved in hexane.

Synthesis of zb CdSe NPLs.[4] To prepare cadmium myristate [$Cd(MA)_2$] as a precursor, 0.24 g NaOH and 1.37 g MA were fully dissolved in 240 ml methanol with 1 h of vigorous stirring. Then, 0.617 g of $Cd(NO_3)_2 \cdot 2H_2O$ was dissolved in 40 ml of methanol and slowly added to the above solution. Subsequently, a white precipitate was obtained. The resulting precipitate was rinsed three times with methanol under vacuum filtration. Finally, it was transferred to a vacuum drying oven at room temperature overnight. The resulting white product is $Cd(MA)_2$. For the synthesis of NPLs, 240 mg of $Cd(OAc)_2 \cdot 2H_2O$, 150 μL of OA and 15 ml of ODE were degassed in a three-necked flask for one hour at 80 °C. Then we raised the temperature to 180 °C and quickly injected 150 μL of TOP-Se (1 M). After washing three times with toluene, the products were dispersed in toluene.

3. Synthesis of photosensitive molecules: PAmG-BTA

A solution of EDC (1.05 g) in anhydrous DCM (40 mL) was added to a solution of trans-o-coumaric acid (0.90 g) in anhydrous THF (5 mL). n-Butylamine (0.49 mL) was then added to the mixture with stirring at room temperature. The mixture turned yellow immediately. After stirring overnight, water was added to quench the reaction and the organic layer was washed with 10% HCl, saturated $NaHCO_3$ and water for each, followed by drying with sodium sulfate. After evaporating the solvent, chloroform was used for recrystallization to give PAmG-BTA as a white crystal. ^{1}H NMR (400 MHz, d-DMSO, δ ppm): 0.89 (3H, t), 1.32 (2H, m), 1.44 (2H, m), 3.17 (2H, m), 6.66 (1H, d), 6.82 (1H, t), 6.89 (1H, d), 7.17 (1H, t), 7.42 (1H, d), 7.63 (1H, d), 8.02 (1H, t).

4. Surface treatment procedures to form ILANs

The NC surface treatment was achieved through both one-phase and two-phase systems. In one-phase system, 1 mL of NC solution (2-10 mg/mL in toluene) was mixed with 100 μL of cation ligand solution (0.2-0.5 M). The resulting mixture was vigorously stirred or shaken until a precipitate of NCs was observed. After centrifugation, the precipitate was redissolved into polar solvents (DMF, NMF, DMSO, PC, etc.). The clear solution was precipitated one more time by adding toluene. The dried powder was then easily redispersed in pure polar solvents to form a stable solution with high concentration (10-60 mg/mL). In the two-phase system, 1 mL of NC hexane solution (2-10 mg/mL) was added to a cation ligand solution (1 mL, 0.02-0.05 M in polar solvents) to form a two-phase mixture.

After vigorous stirring, the hexane layer turned from dark to colorless, while the polar solvent layer turned to color, indicating that the NCs were completely transferred to the polar phase after ligand exchange. The NCs were then purified by hexane, and precipitated from polar solvent by adding a nonsolvent such as acetonitrile or toluene. After centrifugation, NCs were redispersed in various polar solvents to form highly concentrated colloidal solutions (10-60 mg/mL).

5. Secondary surface modification

ILANs can be remodified by organic ligands through both a one-phase system and two-phase system. In the one-phase system, 1 mL of ligand solution (0.02-0.1 M, toluene/hexane for OA or oleylamine and water for MPA) was added to NCs precipitated from polar solvent by centrifugation. After vigorous stirring, remodified NCs were dispersed, forming a colloidal solution. EtOH was used to wash NCs for one more time to remove free ligands. In the two-phase system, 1 mL of ligand solution (0.02-0.1 M in hexane) was mixed with 1 mL of NC colloidal solution (2-10 mg/mL). After vigorous stirring, the NCs transferred into hexane phase, indicating that the NCs were completely remodified by organic ligands. The resulting NC colloidal solution was washed one more time with EtOH.

6. Characterizations

UV-Vis absorption spectroscopy was measured on an Agilent Cary 5000 Spectrophotometer.

The absolute PLQY was measured by using an instrument combining an integrating sphere and a computer-controlled spectrometer (Labsphere).

Time-resolved PL was measured on a HORIBA FL-3 3D Fluorescence Spectrometer.

Fourier transform infrared (FTIR) spectra were acquired in the transmission mode or ATR mode using a Nicolet iS50 FTIR spectrometer.

For **NMR** analysis, 5 mg of NC solids were dissolved in $CDCl_3$ or d_6-DMSO and the signals were recorded on a Bruker AVANCE III-500 spectrometer.

Zeta potential was measured with a Malvern Nano-Z Zeta-Potential Analyzer. A JEOL JEM-2800 transmission electron microscope (TEM) was employed for TEM investigations.

To measure **ECL spectroscopy**, NCs were drop-coated on a Pt electrode. Pt wire and Ag/AgCl were the counter electrode and reference electrode, respectively. The electrolyte was 0.1 mol/L phosphate buffered saline (PBS, pH=7.4) containing 50 mmol/L $K_2S_2O_8$. ECL spectra were measured at -2.0 V (vs. Ag/AgCl).

ICP-OES was measured on a Shimadzu ICPE-9810 Multitype ICP Emission Spectrometer. Samples for ICP-OES measurement were prepared by digesting samples in aqua regia.

7. DOLFIN process

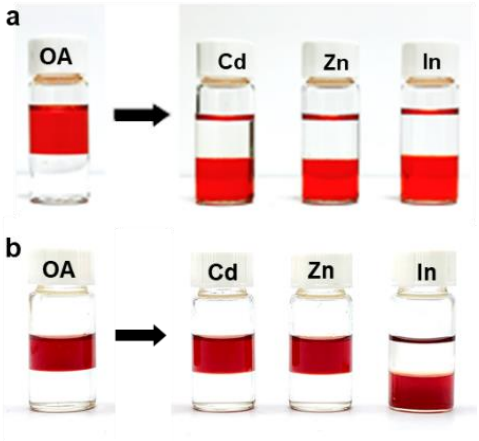
The experiments were performed in a clean room under yellow light. The 12 mm × 12 mm

substrates (Si/SiO_2, Si, quartz, glass) were treated by piranha (conc. H_2SO_4 and 30% H_2O_2, 7:3 v/v) followed by ultrapure water. Photoactive NC inks were passed through a 0.22 μm PTFE filter before use. In a general DOLFIN procedure, 20 μL of ILANs (25 mg/mL in DMF) mixed with PAmG-BTA was dropped onto the substrate and spin-coated (spread: 500 rpm, 10 s; spin: 2000 rpm, 60 s). The DUV light was provided by a low-pressure Hg lamp (254 nm, 3.6 mW/cm^2). The film was exposed through a mask held together in a Mask Aligner system or by using binder clips. After exposure, the film was developed in DMF or NMF to remove unexposed ILANs and unreacted PAmG-BTA molecules. The exposure doses and related parameters for patterning of NCs are listed in Table S1.

8. Inkjet printing process

NCs modified by MPA or CA were dissolved in water mixed with 20% ethylene glycol (v/v). Ethylene glycol was added to control the viscosity and volatility of QD inks, which should be necessary to avoid possible nozzle clogging caused by solvent volatilization.[5] The concentration can be 5–10 mg/mL. The ink-jet printing was taken on the dark parchment by using an HP DeskJet 2130 printer. To obtain brighter patterns, the printing process can be repeated several times.

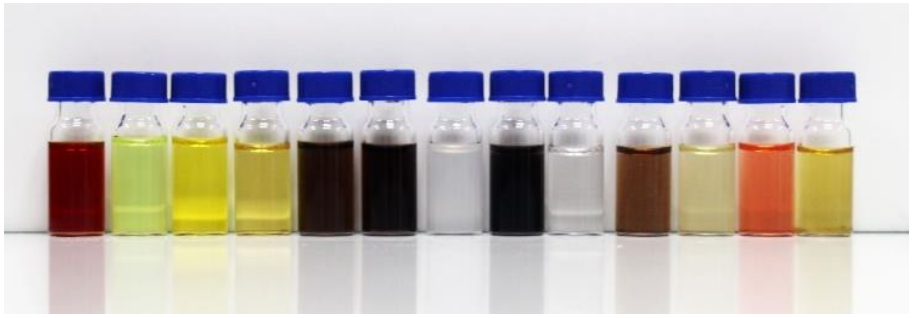
9. Supplementary information of ILANs



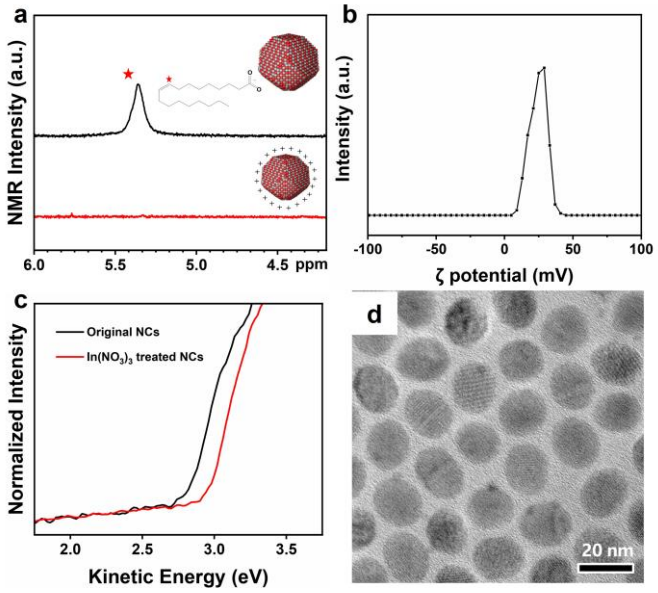
Supplementary Figure 1. Optical images of (a) CdSe NCs and (b) InP NCs before and after treatment with Cd^{2+}, Zn^{2+} and In^{3+} salts. The solvents of upper layer and bottom layer were hexane and DMF, respectively.

According to the hard-soft acid base (HSAB) theory, the driving force of the surface ligand exchange is that cations of metal salts have a stronger binding affinity with organic ligands than NC surface cations. This means that for a given metal cation salt, it is not possible to use it to remove organic ligands from NCs with the same metal element composition (for example, Cd^{2+} or Zn^{2+} salts are not capable of the surface treatment of CdSe NCs or ZnSe NCs, respectively). However, our experiments indicated that In^{3+}, Zn^{2+} and Cd^{2+} salts are also available for converting NCs composed by the

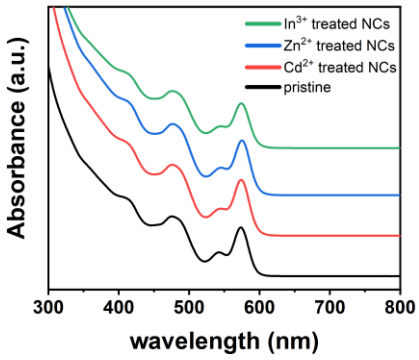
corresponding metal element (Table 1, Figure S1), which requires only a longer time or higher concentration of salts. This discrepancy could be explained by the "softening" phenomenon in binary NCs. The bonds between metal (M) and nonmetal (E) ions of II-VI and III-V NCs are slightly covalent, resulting in an increase in the number of electrons on metal ions (e.g., Cd^{2+} to $Cd^{(2-n)+}$ in the case of CdSe NCs). According to the definitional formula of η, the absolute hardness decreases as N increases. Therefore, the surface Cd^{2+} cations are slightly softer than isolated Cd^{2+} cations. The same phenomenon was also observed in InP NCs and reported by Nag et al. in previous literature[6].



Supplementary Figure 2. Colloidal solutions of the all-inorganic NCs. From left to right: CdSe, CdZnSeS/ZnS, CdSe/ZnS, CdSe/CdS, PbS, Fe_2O_3, TiO_2, FePt, $NaYF_4$, CdSe nanowires, CdSe nanoplatelets (wurtzite), CdSe nanoplatelets (zinc-blende), Ag NCs.



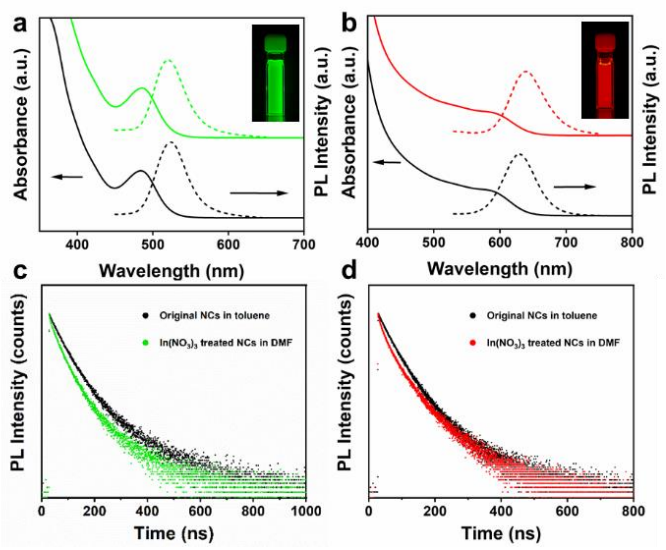
Supplementary Figure 3. Supplementary characterizations of ILANs. (a) 1HNMR spectra of OA-capped and $In(NO_3)_3$-treated CdSe/CdZnSeS/ZnS NCs. (b) ζ-potential measurement of $In(NO_3)_3$-treated CdSe/CdZnSeS/ZnS NCs. (c) UPS (secondary electron cutoff regions) of OA-capped NCs and $In(NO_3)_3$ treated CdSe/CdZnSeS/ZnS NCs. (d) TEM images of CdSe/ZnS NCs capped by OA.



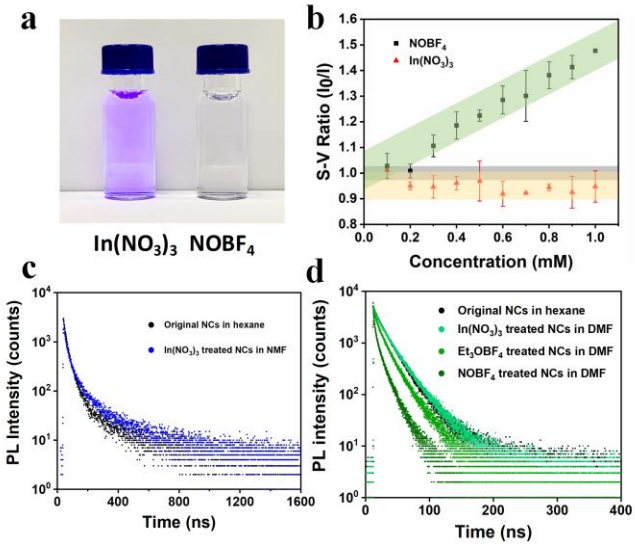
Supplementary Figure 4. Absorption spectra of CdSe NCs before and after treatment with Cd^{2+}, Zn^{2+} and In^{3+} salts. The signals at 573 nm, 542 nm and 475 nm belong to the first excitonic transition ($1S_{3/2}$-1Se) and other higher-energy transitions of 3.6-nm CdSe QDs.

Supplementary Table 1. QY and lifetime of NCs capped with OA and treated with $In(NO_3)_3$

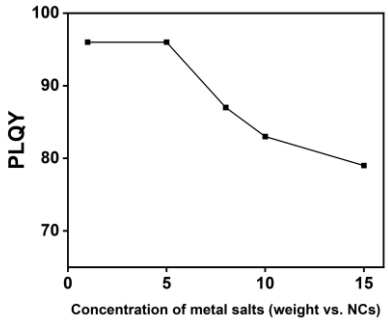
NCs	OA		$In(NO_3)_3$	
	QY	Lifetime	QY	Lifetime
CdSe/ZnS (red)	97%	24 ns	97%	24 ns
CdSe/CdZnSeS/ZnS (green)	84%	18 ns	80%	18 ns
CdZnS/ZnS (blue)	82%	38 ns	72%	34 ns
InP/ZnSeS/ZnS (red)	66%	45 ns	39%	40 ns
InP/ZnSeS/ZnS (green)	76%	64 ns	57%	48 ns



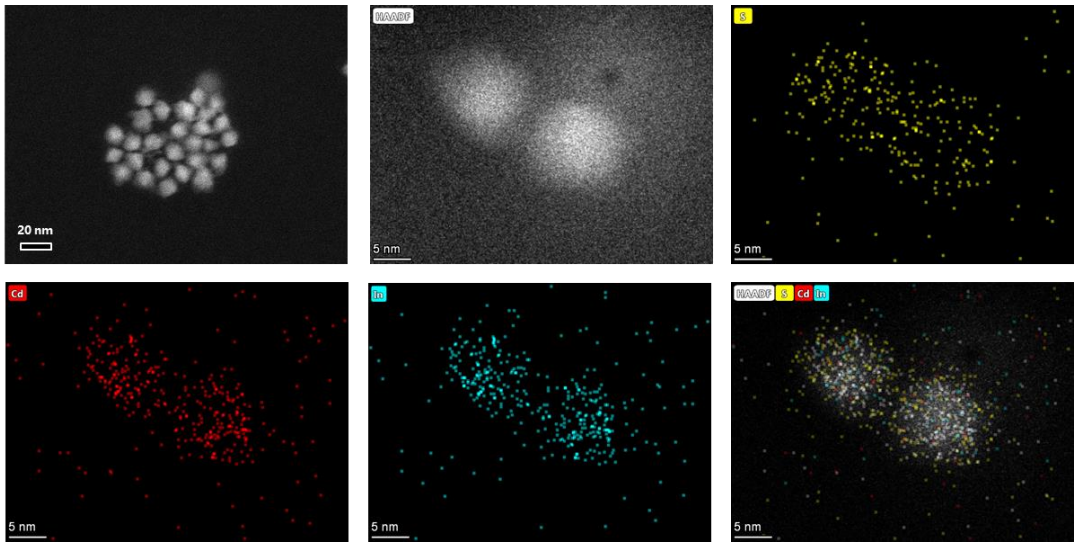
Supplementary Figure 5. Absorption, PL spectra (a, b) and transient PL kinetics (c, d) of green and red-emitting InP/ZnSeS/ZnS NCs before (dark lines) and after (colorful lines) treatment with $In(NO_3)_3$.



Supplementary Figure 6. Supplementary optical measurements of ILANs. (a) Optical image of blue-emitting NCs treated with $In(NO_3)_3$ and $NOBF_4$ (photographed under UV light). (b) Stern-Volmer ratio of CdSe/CdZnSeS/ZnS NCs treated with $NOBF_4$ and $In(NO_3)_3$ at concentrations from 0 to 1 mM. (c, d) Transient PL kinetics of blue and green NCs treated with different inorganic ligands.



Supplementary Figure 7. The PLQYs of red-emitting CdSe/ZnS NCs treated by $In(NO_3)_3$ with various concentration.

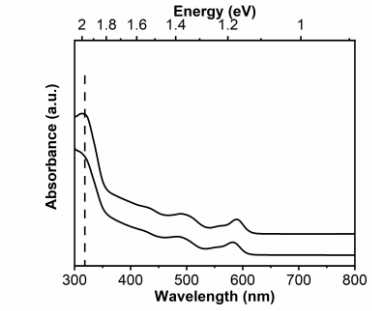


Supplementary Figure 8. Scanning transmission electron microscopy (STEM) image and energy dispersive spectroscopy (EDS) mapping images of $In(NO_3)_3$ treated CdSe/ZnS NCs.

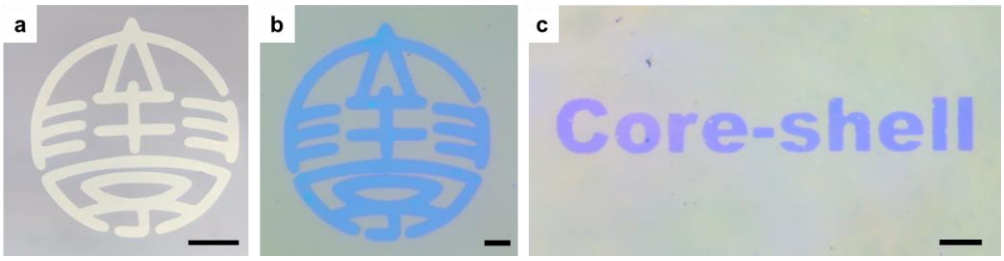
10. Supplementary information of patterning

Supplementary Table 2. Patterning conditions of PAmG-assisted DOLFIN

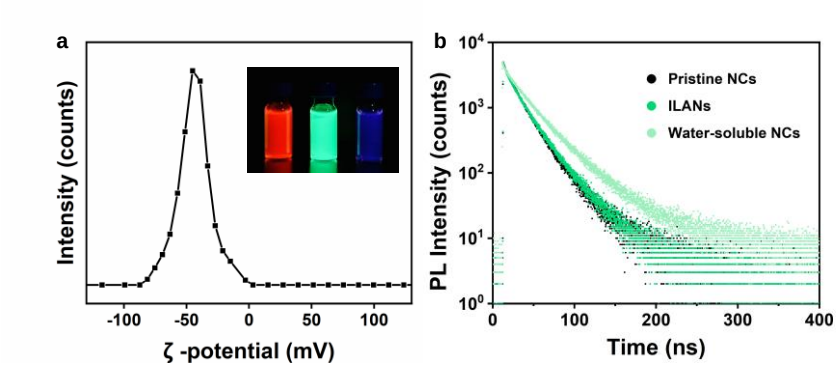
NCs	Concentration (mg/mL)	PAmG-BTA (wt, vs. NCs)	Ink Solvent	Developers	Dose (254 nm, mJ/cm^2)
CdSe	20	0.2	DMF	DMF, NMF	45-120
ZnSe	20	0.2	DMF	DMF, NMF	45-90
PbS	20-30	0.2	DMF	DMF, NMF	45-90
CdSe/ZnS	20-30	0.4	DMF	NMF	80-110
CdSe/CdZnSeS/ZnS	20-30	0.4	DMF	NMF	80-110
CdZnS/ZnS	20-30	0.4	DMF	NMF	80-110
InP/ZnS	20	0.4	DMF	NMF	80-110



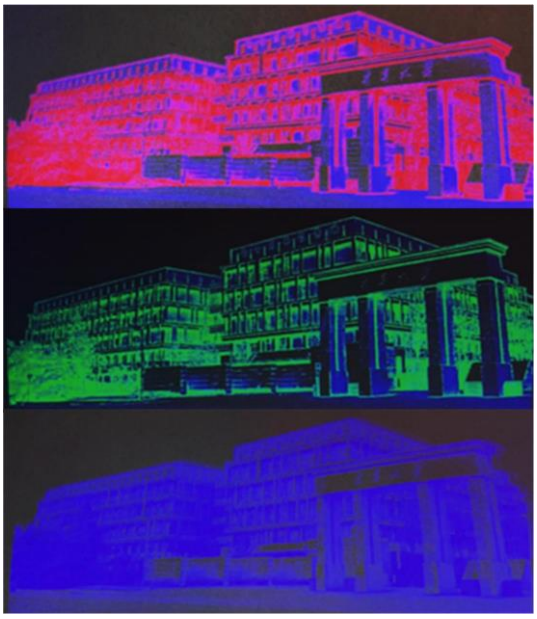
Supplementary Figure 9. Absorption spectra of CdSe NCs mixed with PAmG-BTA before (upper line) and after (lower line) photodecomposition.



Supplementary Figure 10. Optical images of (a) PbS NC (b) ZnSe NC, and (c) InP/ZnS NC patterns via PAmG-assisted DOLFIN. Scale bar: (a) 50 μm; (b) 10 μm; (c) 10 μm.

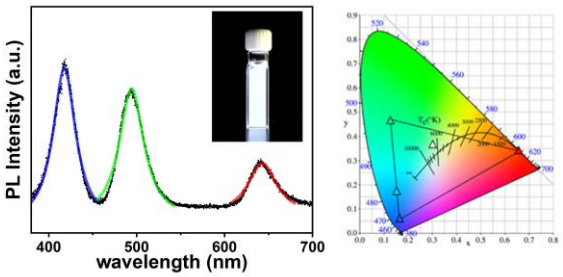


Supplementary Figure 11. Water-soluble NCs. (a) ζ-potential measurement of ILANs modified by MPA. Inset: optical image of the red, green and blue nanoinks. (b) PL decay curves of MPA-modified NCs compared with original and all-inorganic NCs. The PLQY of MPA-modified green-emitting CdSe/CdZnSeS/ZnS NCs was 91% in water, and the lifetime was 27 ns.



Supplementary Figure 12. Single-color ink-jet printing of blue, green and red NCs.

The white ink for the panda face was prepared by mixing red, green and blue inks in an appropriate proportion. The colloidal stability of the postmodified ILANs was not influenced after mixing with each other (Figure S10a, inset). Figure S11a provides the PL spectrum of the white ink, containing the emission features of red, green and blue. Converted from the PL spectrum, the CIE coordinate of the white is at the center of the red-green-blue triangle with a color temperature of ~6500 K (Figure S11b). Cyan, the background color of the panda image, was obtained by mixing blue and green inks, so the coordinate of cyan is on the connecting line between blue and green (Figure S11b). The areas with different colors in the fluorescent panda image had distinct edges, suggesting a high precision of the ink-jet printing.



Supplementary Figure 13. The PL spectrum and CIE coordinates of the white nanoink. The three emission peaks can be fitted into red, green and blue features. Inset: optical image of white ink.

References

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