

Time-resolved color-changed long-afterglow for security systems based on metal-organic hybrids

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General Information and Materials. All the materials and reagents were obtained from commercial channels and were analytically pure. Infrared spectra data were measured on a BRUKER TENSOR 27 spectrophotometer with KBr pellets (400–4000 cm^{-1}). All elemental analysis (C, H, and N) were performed on a FLASH EA 1112 instrument. Powder X-ray diffraction (PXRD) data were measured on a Bruker D8 VENTURE diffractometer with Cu- $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The steady-state spectra (fluorescence and phosphorescence) for the solid samples were recorded on a HITACHI F-4600 fluorescence spectrophotometer at room temperature. The lifetimes and phosphorescence absolute quantum yields were measured by a FLS980 fluorescence spectrometer. All videos were recorded on a Sony HDR-XR160E digital video camcorder.

Crystal Data Collection and Refinement. Single crystal of **Himpc-HNO₃**, **Cd-impc** and **Zn-impc** with high quality were selected. Their X-ray diffraction data were collected on a Bruker SMART APEX-II CCD diffractometer¹ employing Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at $298 \pm 1 \text{ K}$. The structures of three crystals were solved with the SHELXS-97 crystallographic software package and refined through the SHELXL-2014 programs.^{2,3} All nonhydrogen atoms were refined anisotropically.

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Synthesis of $(\text{Himpc}\cdot\text{HNO}_3)_n$ (Himpc-HNO₃**).** Single crystals of **Himpc-HNO₃** qualified for X-ray crystallography were obtained through liquid-liquid diffusion method. Himpc (0.2g) was dissolved in 80 mL methanol, and the concentrated nitric acid was slowly dropped into the solution until it became clear, and then the concentrated nitric acid (8 mL) was added into above solution. After that, the ether (80 mL) was slowly added along the side of the beaker. The solution was sealed and refrigerated for two or three days, a large number of colorless and transparent sheet-shaped crystals were obtained. The crystals of **Himpc-HNO₃** were filtered and dried in the air at room temperature (yield: 74%, based on Himpc). Elemental Anal. Calcd. for $\text{C}_9\text{H}_8\text{N}_4\text{O}_5$: C, 42.86; H, 3.20; N, 22.22 (%). Found: C, 41.44; H, 2.98; N, 21.75 (%). IR (KBr pellet, cm^{-1}): 3127s, 3058s, 2849s, 2627s, 1950w, 1717s, 1600w, 1545m, 1402s, 1339s, 1253s, 1170m, 1114m, 1024w, 904m, 841m, 771s, 698s, 531w, 423w.

Synthesis of $[\text{Cd}(\text{impc})_2(\text{H}_2\text{O})_2]_n$ (Cd-impc**).** **Cd-impc** was synthesized according to the procedure described in the previous literature.⁴ The yield (70%, based on Cd) was higher than that reported. Elemental Anal. Calcd. For $\text{C}_{18}\text{H}_{16}\text{CdN}_6\text{O}_6$: C, 41.16; H, 3.05; N, 16.01 (%). Found: C, 41.13; H, 3.12; N, 15.97 (%). IR (KBr pellet, cm^{-1}): 3095w, 1951s, 1883s, 1575w, 1320w, 1171m, 1105w, 1031m, 995m, 975s, 883w, 771w, 676w, 564m, 534m, 447m.

Synthesis of $\{[\text{Zn}(\text{impc})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}\}_n$ (Zn-impc**).** A mixture of $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ (0.03 mmol, 8.6 mg) and Himpc (0.03 mmol, 5.7 mg) was dissolved in a mixed solvent of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (3:1 by volume, 4 mL), stirred for 10 min to form a homogeneous solution, and then sealed in a 25 mL Teflon-lined stainless steel vessel. The mixture was slowly heated at 120°C for 72 h and then cooled to room temperature at a rate of $5^\circ\text{C}\cdot\text{h}^{-1}$. Colorless block crystals of **Zn-impc** were filtered, dried in the air at room temperature (yield: 67%, based on Zn). Elemental Anal. Calcd. For $\text{C}_{18}\text{H}_{28}\text{ZnN}_6\text{O}_{10}$: C, 39.32 H, 4.40; N, 15.29 (%). Found: C, 39.76; H, 4.00; N, 15.73 (%). IR (KBr pellet, cm^{-1}): 3119w, 1908s, 1565w, 1390w, 1281w, 1242m, 1026s, 996m, 903w, 866w, 759w, 656w, 581m, 507m, 426s.

(a)

(b)

Scheme S1. The coordination modes of **impc⁻** liands in compounds: (a) **Cd-impc** and (b) **Zn-impc**.

Structural description of **(Himpc·HNO₃)_n (Himpc-HNO₃)**.

Single crystal X-ray analysis reveals that **Himpc-HNO₃** crystallizes in the monoclinic system with space group $P2_1/n$. As illustrated in Figure S1a, the asymmetric unit of **Himpc-HNO₃** possesses one Himnc ligand and one HNO₃ molecule. With assistance of HNO₃, the adjacent Himpc molecules are linked through strong intermolecular hydrogen bonds {O1–H1···O4 [H/O distances (bond angles): 1.83 Å (152.0°)], O5–H5···N1 [H/N distances (bond angles): 1.94 Å (174.5°)]} forming 1D chains running along the *b* axis which are further packed into a 2D layer structure by intermolecular hydrogen bonds C7–H7···O4 [H/O distances (bond angles): 2.46 Å (154.6°)], C8–H8···O3 [H/O distances (bond angles): 2.44 Å (138.5°)] and C9–H9···O1 [H/O distances (bond angles): 2.56 Å (167.4°)] (Fig. S1b). The 2D layers are further extended into a 3D supramolecular structure by C6–H6···N3 [H/N distances (bond angles): 2.55 Å (172.9°)] and C3–H3···O2 [H/O distances (bond angles): 2.57 Å (140.9°)]. Additionally, between pyridine and imidazole ring of the interlayered **impc⁻** ligands, the C–H··· π short connects with a *ca.* 3.43 Å distance of H4 to the neighboring imidazole rings (H4/ π -plane separation: 3.43 Å, dihedral angle: 49.24°) further stabilize the 3D structure (Figure S1c).

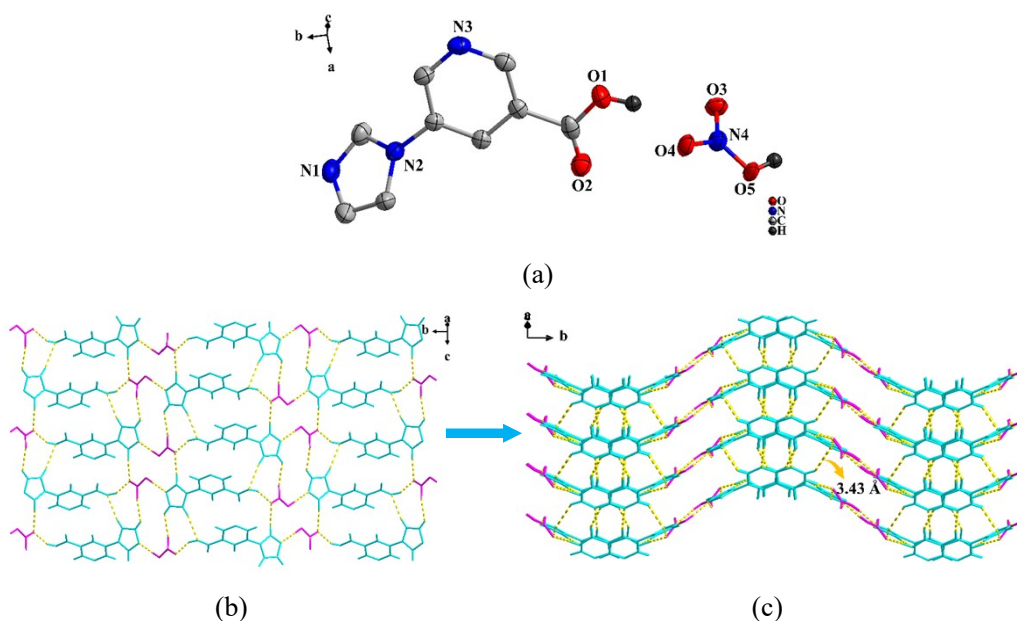
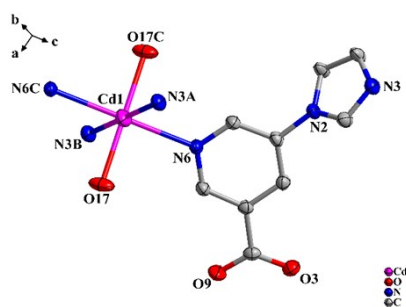


Figure S1. (a) The asymmetric unit of **Himpc-HNO₃** crystal, partial hydrogen atoms are omitted for clarity. (b) The 2D layer structure running along the *bc* plane. (c) View of the 3D assembly of **Himpc-HNO₃**. Intermolecular hydrogen bonds marked by dotted lines.

Structural description of [Cd(imnc)₂(H₂O)₂]_n (**Cd-impc**).

Single-crystal X-ray diffraction reveals that **Cd-impc** crystallizes in the triclinic system with the *P-1* space group. It should be noted that the structure of **Cd-impc** has been reported, and the specific description of its crystal structure is omitted.⁴ Herein, we only point out the spatial arrangement and intermolecular interactions in **Cd-impc**. In **Cd-impc**, the adjacent Cd(II) ions are bridged by **impc**⁻ ligands to form an infinite one-dimensional chain with the nonbonding Cd···Cd distance of 9.07 Å. These 1D chains are stacked into extended 2D supramolecular structure through $\pi \cdots \pi$ interactions between two interchain pyridine rings with center-to-center separation: 3.57 Å (interplanar separation of 3.40 Å) and C–H··· π attractions with a *ca.* 3.15 Å distance of H9 to the neighboring imidazole rings (H9/ π -plane separation: 3.15 Å, dihedral angle: 53.32°) along the *ac* plane (Fig. S2b), which are further extended to a 3D framework through hydrogen bonds C1–H1···O9 [H/O distances (bond angles): 2.38 Å (151.5°)], C3–H3A···O3 [H/O distances (bond angles): 2.34 Å (155.3°)] and C11–H11···O9 [H/O distances (bond angles): 2.55 Å (155.0°)] (Fig. S2c).



(a)

(b)

(c)

Figure S2. (a) The coordination environment around the Cd(II) atom in **Cd-impc** (symmetry codes for A: $-x, -y, 1-z$; B: $1+x, 1+y, z$; C: $1-x, 1-y, 1-z + 1$), all hydrogen atoms are omitted for clarity. (b) 2D structure constructed via $\pi \cdots \pi$ and C-H $\cdots\pi$ interactions. (c) View of the 3D packing structure. Intermolecular interactions are denoted by dotted lines.

Structural description of $\{[\text{Zn}(\text{impc})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}\}_n$ (**Zn-impc**).

Single crystal X-ray diffraction analysis reveals that **Zn-impc** is a mononuclear complex which crystallizes in the monoclinic system with space group $P2_1/n$. There is one crystallographically independent Zn(II) ion, two **impc**⁻ ligands, four coordinated water molecules, and two lattice water molecules in the asymmetric unit. As shown in Fig. S3a, each six-coordinated Zn(II) ion is in a distorted octahedral coordination geometry by two pyridine nitrogen atoms (N3, N3A) from one **impc**⁻ ligand and four oxygen atoms (O3, O4, O3A, O4A) from four coordination water molecules, in which, the equatorial plane comprises four monodentate coordinate oxygen atoms (O3, O3A, O4, O4A) from four coordination water, and the apical sites are occupied by two monodentate coordinate imidazole nitrogen atoms (N3, N3A) from two indistinguishable **impc**⁻ ligands (N3–Zn–N3A angle of 180°). The Zn–O bond lengths vary from 2.154(1) to 2.190(1) Å, the Zn–N bond lengths is equal to 2.075(1) Å, and the angles around Zn(II) are in the range of 88.00(5)° to 180°, which are in good accordance with the reported Zn(II) complexes.⁵⁻⁷ Furthermore, there are abundant solvent water molecules in the unit cell of **Zn-impc** calculated by PLATON software, and further confirmed by TGA and elemental analysis. Thus, a large number of

intermolecular hydrogen bonds exist between neighboring **impc**⁻ ligands and surrounding water molecules, which contribute to construct a 3D supramolecular structure. The 3D structure of **Zn-impc** is further stabilized by the π -stacking interactions, including C–H $\cdots\pi$ attractions (H6/ π -plane separation: 2.88 Å and H1/ π -plane separation: 3.36 Å, respectively, dihedral angle: 82.72°) between two neighboring imidazole and pyridine rings, and $\pi\cdots\pi$ interactions with a centroid-to-centroid separation of 3.49 Å (the vertical distance is 3.30 Å) between two adjacent pyridine rings of **impc**⁻ ligands (Fig. S3b).

(a)

(b)

Figure S3. (a) The surrounding coordination environment of **Zn-impc** (symmetry codes for A: 1-x, -y, 1-z), all hydrogen atoms are omitted for clarity. (b) 3D packing arrangement, C–H $\cdots\pi$ and $\pi\cdots\pi$ interactions are denoted by dotted lines.

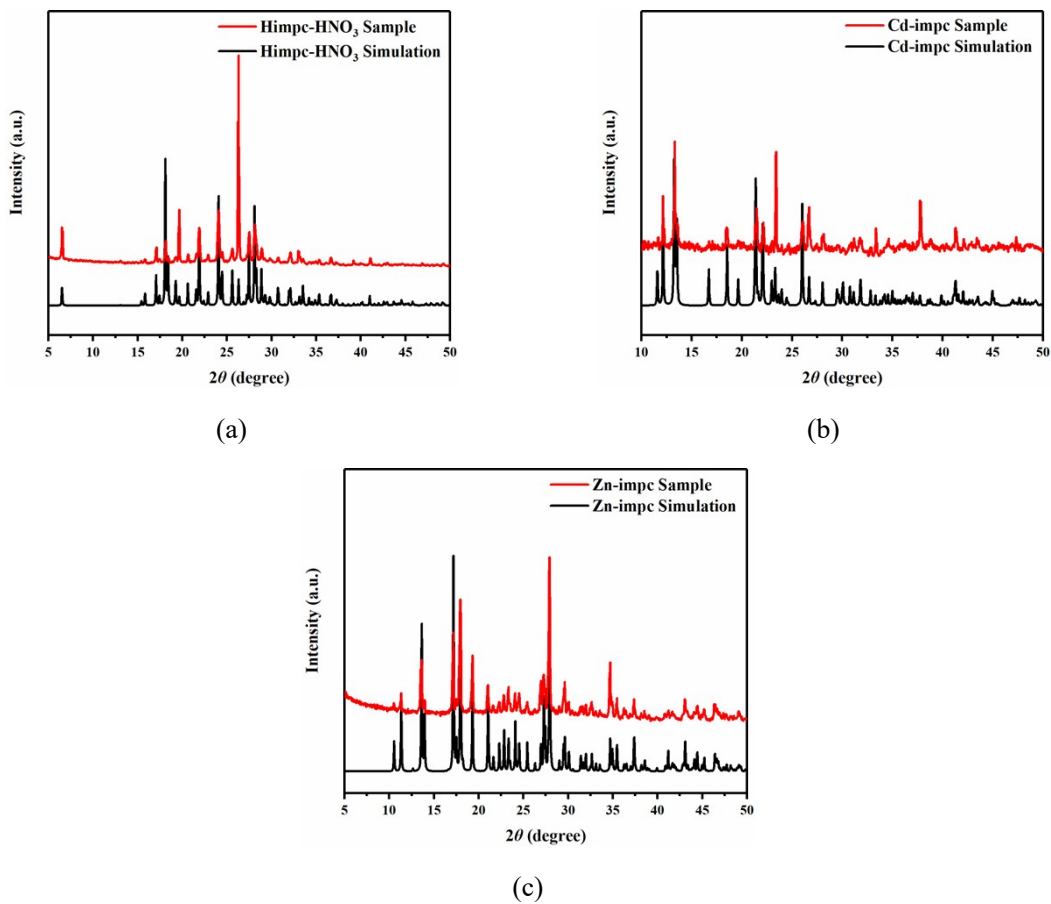


Figure S4. PXRD patterns for simulated and experimental samples: (a) **Himpc-HNO₃**, (b) **Cd-impc**, and (c) **Zn-impc**.

Table S1. The processing parameters and crystallographic data for **Himpc-HNO₃**, **Cd-impc** and **Zn-impc**.

Compounds	Himpc-HNO₃	Cd-impc	Zn-impc
Formula	C ₉ H ₈ N ₄ O ₅	C ₁₈ H ₁₆ CdN ₆ O ₆	C ₁₈ H ₂₄ ZnN ₆ O ₁₀
Formula weight	252.19	524.78	549.80
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P2₁/n</i>	<i>P-1</i>	<i>P2₁/n</i>
<i>a</i> (Å)	6.2551(7)	7.8039(5)	8.7580(4)
<i>b</i> (Å)	27.076(3)	8.4162(5)	12.6849(6)
<i>c</i> (Å)	6.4618(7)	8.6025(5)	10.3307(5)
<i>α</i> (deg)	90	101.523(1)	90
<i>β</i> (deg)	100.786(4)	108.064(1)	106.741(2)
<i>γ</i> (deg)	90	112.127(1)	90
<i>V</i> (Å ³)	1075.1(2)	464.34(5)	1099.04(9)
<i>Z</i>	4	1	2
Dc (g·cm ⁻³)	1.558	1.877	1.661
F(000)	520	262	568
θ range for data collection (deg)	3.296–28.298	3.097–28.319	3.136–27.631
Reflections collected/unique	17861/2610	13005/2312	26234/2532
Data/restraints/params	2610/0/164	2312/0/156	2532/0/160
Goodness-of-fit on F ²	1.057	0.862	1.010
Final <i>R_I</i> ^a , <i>wR₂</i> ^b	0.0830, 0.2460	0.0188, 0.0491	0.0303, 0.0727

$$^a R_I = \frac{|F_o| - |F_c|}{|F_o|}, \quad ^b wR_2 = [w(|F_o^2| - |F_c^2|)^2 / w|F_o^2|^2]^{1/2}.$$

Table S2. Selected bond lengths (Å) and angles (deg) for **Cd-impc** and **Zn-impc**.

Cd-impc					
Cd(1)–O(17)	2.264(1)	Cd(1)–N(3)#3	2.340(1)	Cd(1)–N(6)#1	2.397(1)
Cd(1)–O(17)#1	2.264(1)	Cd(1)–N(6)	2.397(1)	Cd(1)–N(3)#4	2.340(1)
Cd(1)–N(3)#2	2.340(1)	O(17)–Cd(1)–O(17)#1	180	O(17)–Cd(1)–N(3)#2	90.87(6)
O(17)#1–Cd(1)–N(3)#2	89.13(6)	O(17)#1–Cd(1)–N(3)#3	90.87(6)	O(17)–Cd(1)–N(6)	90.39(5)
O(17)–Cd(1)–N(3)#3	89.13(6)	N(3)#2–Cd(1)–N(3)#3	180.00(6)	O(17)#1–Cd(1)–N(6)	89.61(5)
N(3)#2–Cd(1)–N(6)	83.73(5)	O(17)–Cd(1)–N(6)#1	89.61(5)	N(3)#2–Cd(1)–N(6)#1	96.27(5)
N(3)#3–Cd(1)–N(6)	96.27(5)	O(17)#1–Cd(1)–N(6)#1	90.39(5)	N(3)#3–Cd(1)–N(6)#1	83.73(5)
N(6)–Cd(1)–N(6)#1	180				
Zn-impc					
Zn(1)–N(3)	2.075(1)	Zn(1)–O(3)	2.154(1)	Zn(1)–O(4)#1	2.190(1)
Zn(1)–N(3)#1	2.075(1)	Zn(1)–O(3)#1	2.154(1)	Zn(1)–O(4)	2.199(1)
N(3)–Zn(1)–O(3)	91.52(6)	N(3)–Zn(1)–O(3)#1	88.48(6)	N(3)–Zn(1)–O(4)	88.00(5)
N(3)#1–Zn(1)–O(3)	88.48(6)	N(3)#1–Zn(1)–O(3)#1	91.52(6)	N(3)#1–Zn(1)–O(4)	92.00(5)
O(3)–Zn(1)–O(4)#1	88.12(5)	O(3)–Zn(1)–O(3)#1	180	O(3)–Zn(1)–O(4)	91.88(5)
O(3)#1–Zn(1)–O(4)#1	91.88(5)	N(3)–Zn(1)–O(4)#1	92.00(5)	O(3)#1–Zn(1)–O(4)	88.12(5)
N(3)–Zn(1)–N(3)#1	180	N(3)#1–Zn(1)–O(4)#1	88.00(5)	O(4)#1–Zn(1)–O(4)	180

Symmetry transformations used to generate equivalent atoms:

For **Cd-impc**: #1: -x+1, -y+1, -z+1; #2: -x, -y, -z+1; #3: x+1, y+1, z; #4: x-1, y-1, z.

For **Zn-impc**: #1: -x+1, -y, -z+1.

Table S3. Hydrogen bonds in **Himpc-HNO₃**, **Cd-impc** and **Zn-impc**.

D–H···A	d(D–H)/Å	d(H···A)/Å	d(D–A)/Å	∠(DHA)/°
Himpc-HNO₃				
O(5)–H(5)···N(1)	0.82	1.94	2.756(45)	174.5
C(8)–H(8)···O(3)	0.93	2.44	3.198(57)	138.5
O(1)–H(1)···O(4)	0.90	1.83	2.665(41)	152.0
C(7)–H(7)···O(4)	0.93	2.46	3.326(55)	154.6
C(6)–H(6)···N(3)	0.93	2.55	3.470(36)	172.9
C(3)–H(3)···O(2)	0.93	2.57	3.343(141)	140.9
C(9)–H(9)···O(1)	0.93	2.56	3.476(47)	167.4
Cd-impc				
C(11)–H(11)···O(9)#5	0.95	2.55	3.437(2)	155
C(3)–H(3A)···O(3)#6	0.95	2.34	3.225(2)	155.3
C(1)–H(1)···O(9)#7	0.95	2.38	3.245(2)	151.5
Zn-impc				
O(5)–H(5W)···O(1)	0.91	2.61	3.264(2)	129.2
O(5)–H(5W)···O(2)	0.91	1.87	2.715(2)	152.8
O(5)–H(5WA)···O(4)#2	0.89	2.00	2.882(2)	176.2
O(3)–H(3WA)···O(5)#3	0.93	1.86	2.780(2)	172.5
O(4)–H(4)···N(1)#4	0.91	1.85	2.744(2)	167.4
C(2)–H(2)···O(1)#5	0.93	2.61	3.476(2)	154.3
C(5)–H(5)···O(1)#6	0.93	2.61	3.102(2)	113.3
C(3)–H(3)···O(5)#3	0.93	2.17	3.087(2)	166.5
C(9)–H(9)···O(2)#2	0.93	2.59	3.432(2)	151.6

Symmetry transformations used to generate equivalent atoms:

For **Himpc-HNO₃**: -.For **Cd-impc**: #1: -x+1, -y+1, -z+1; #2: -x, -y, -z+1; #3: x+1, y+1, z; #4: x-1, y-1, z; #5: -x+2, -y+1, -z+2; #6: -x+1, -y, -z+2; #7: -x+1, -y+1, -z+2.For **Zn-impc**: #1: -x+1, -y, -z+1; #2: -x+1, -y+1, -z+1; #3: -x+1, y-1/2, -z+3/2; #4: x-1, -y+1/2, z-1/2; #5: -x+2, -y+1, -z+1; #6: -x+2, y-1/2, -z+3/2.

Table S4. Photophysical properties of **Himpc**, **Himpc-HNO₃**, **Cd-impc** and **Zn-impc**.

Sample	Fluorescence						Phosphorescence						
	λ_{em} (nm)	m	τ_i (ns)	A_i (%)	$\langle\tau\rangle$	χ^2	λ_{em} (nm)	m	τ_i (ms)	A_i (%)	$\langle\tau\rangle$ (ms)	χ^2	Φ_P (%)
Himpc	465	1	7.1	100	7.1	1.13			0.4	30			0.4
							510	3	1.5	46	2.2	1.28	
									5.9	24			
Himpc-HNO₃	400	1	4.5	100	4.5	1.24	600	1	32	100	32	1.22	1.75
							485	2	4.3	60	9.1	1.01	
									16.3	40			
Cd-impc	450	1	5.4	100	5.4	1.16	550	1	69	100	69	0.95	2.05
							490	1	78	100	78	1.27	
							573	1	370	100	370	1.21	
Zn-impc	460	1	6.8	100	6.8	1.17	504	1	84	100	84	1.02	2.17
							580	1	405	100	405	1.28	

λ_{em} = emission maximum, **m** stands for the i-exponential fitting of the PL decay curve, τ_i is the excited state lifetime, A_i represents the ratio of τ_i . The fitting goodness is manifested by the value of χ^2 which should lower than 1.300. In the i-exponential case, $\langle\tau\rangle = A_1\tau_1 + A_2\tau_2 + \dots + A_i\tau_i$, $A_1 + A_2 + \dots + A_i = 1$. $\langle\tau\rangle$ = mean lifetime, Φ_P = quantum yield of phosphorescence.

Table S5: The comparison of the long-lived lifetime and quantum yield values in ref. [8, 9] and this work under ambient conditions.

Compounds	Lifetime (ms)	Quantum Yield (%)	Ref.
BTA	0.2	-	8
BEA-ME-1	1.0	7.86	8
BEA-ME-2	0.7	5.24	8
4HP	-	10.34	9
CdCl ₂ -4HP	103.12	63.55	9
CdBr ₂ -4HP	1.42	25.36	9
Himpc	32	0.40	This work
Himpc-HNO ₃	69	1.75	This work
Cd-impc	370	2.05	This work
Zn-impc	405	2.17	This work

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