Electronic Supplementary Information

Color-Tunable Ultralong Room Temperature Phosphorescence from EDTA

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Section S1. Experimental Section

S1.1 Materials

The detailed information of the materials was given in Table S1.

Name	CAS No.	Specification	Supplier
		≥99.99%	Aladdin
		≥99%	Adamas beta
EDTA	60-00-4	≥99%	General reagent
		≥99.4%	Alfa aesar
		≥99%	SCRC
			Aladdin
EDTA-Na ₂	6381-92-6		Sigma-Aldrich
		≥99%	General reagent
EDTA-K ₂	25102-12-9	≥99%	Aladdin
EDTA-(NH ₄) ₂	304675-80-7	≥98%	Aladdin
EDTA-Na ₄	10378-23-1	≥99%	Aladdin
EDTA Dianhydride	22011 25 2	>000/	A 1 - 4 J
(EDTAD)	23911-25-3	<u>≥</u> 98%₀	Aladdin
EDTA-Na ₂ -Mg	14402-88-1	≥98.5%	Aladdin
Trigtycolamidic Acid (NTA)	139-13-9	≥99%	Aladdin
Diethylenetriamine	(7.42.6	> 0.00/	A 1 11 ¹
pentaacetic Acid (DTPA)	67-43-6	<u>>99%</u>	Aladdin
Triethylenetetramine	9(0,52,2	>000/	A 1- 4 4
hexaacetic Acid (TTHA)	009-32-3	<u>~</u> 98%0	Alauum
Citric acid (CA)	77-92-9	≥99%	Aladdin
Tartaric acid (TA)	526-83-0	≥99%	JuHuiChemical

S1.2 Apparatus

All the instrumental information used for characterizations were given in Table S2.

Table S2.	The instrumental	information	used in this	work.
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Characterization items	Model	Manufacturer
UV/Vis absorption spectra	Lambda-365	Perkin Elmer, USA
	Fluolog-3 spectrofluorometer	
	Phosphorescence lifetime excitation: Spectral LED: 280 nm, 355	
Phosphorescence lifetime	nm	Horiba Jobin Yvon,
	For collection of the lifetime, bandpass filters were used.	USA
	280 bandpass filter (FF01-280/10-25): 280 ± 5 nm	
	356 bandpass filter (FF01-356/30-25): 280 ± 15 nm	
Fluorescence & phosphorescence	Flueremer 4 exectroflueremeter	Horiba Jobin Yvon,
spectrum	Fluoromax-4 spectronuorometer	USA
	Azure c300	
Chemiluminescence imaging	excitation: LED: 365 nm	AZUIE, USA

S1.3 General experimental details

The phosphorescence spectra were collected with a FluoroMax-4P spectrofluorometer (Horiba Jobin Yvon, USA) with a flash Xe lamp as the excitation (delay time of 10 ms). Phosphorescence lifetime and time-resolved emission spectra (TRES) were measured with a FluroLog-3 spectrofluorometer (Horiba Jobin Yvon, USA) with SpectraLED (280 nm and 355 nm) as the excitation source. During collection of the phosphorescence lifetime, bandpass filters were placed at the excitation slit to eliminate potential interference from the excitation source (280 bandpass filter (FF01-280/10-25): 280 ± 5 nm; 356 bandpass filter (FF01-356/30-25): 280 ± 15 nm).

For collection of the afterglow images, the sample was pelleted and fixed with two quartz slides before putting into the cryogenic chamber (Optistat CF2, Oxford Instrument). Here, due to the extremely weak RTP emission, we collected the afterglow emission images at 77 K with upon exciting at 280 nm and 365 nm (from a 450 W xenon lamp of the FluroLog-3 spectrofluorometer). After glow images were directly taken by a RICOH GR II camera with 0.5 s exposure.

S1.4 Theoretical calculation method

Time-Dependent Density Functional Theory (TD-DFT) is a popular tool to compute the characteristics of electronically ground states and excited states in photo-chemical process. In this work, on the basis of Gaussian 09 software^[1], DFT and TD-DFT theory was applied as the basic principle of theoretical calculations, all the sample structures were fully optimized by M062X with 6-311+g(d) and 6-311g(d) basic set, heavy metal ion was optimized with SSD basic set. Firstly, vertical excitation energies were calculated based on the optimized ground state geometries (S₀). In our system, the electronic excitation could not be presented by a single pair of molecular orbitals (eg: HOMO/LUMO), thus Hole-electron analyze method was adopted to study their excitation characters conveniently. This method can provide a definitive description of electronic excitation process by highlighting where the electrons were excited (Hole) and where the electrons excited to (Electron) through wave function analysis program Multiwfn.^[2] Hole-electron distribution map and molecular orbitals were visualized through VMD, respectively.^[3]

QM/MM calculations were carried out based on ONIOM with Gaussian 09. For the QM part, the center molecule was fully optimized with the M062X with 6-311g(d) basic set. The structure of molecules in the MM part was frozen and governed by UFF mechanical field.

Inter system crossing (ISC) process were further evaluated through ORCA package^[4] (version 4.1.1) with M062X and SDD basic set. The electronic structures and the spin-orbit coupling (SOC) matrix elements between singlet and triplet states were obtained on basis of optimized geometries in S₁ excited state. In essence, the ISC process was determined the spin-orbital coupling (SOC) $\langle T|H_{soc}|S \rangle$ and the energy difference between S₁ and T₁ (ΔE_{ST}):

$$k_{ISC} \propto rac{\xi_{ST}^2}{e^{\Delta E_{ST}^2}}$$

The excited state molecular orbitals and the electronic structures of EDTA, EDTA-Na₂ were further calculated with TD-DFT. SOC constants (ξ) and the singlet-triplet energy gap (ΔE_{ST}) were thus derived to evaluate ISC and phosphorescence process.^[5]

Section S2. Research backgrounds

S2.1 Crystal information about previous clusteroluminogens

Table S3. Summary of the existing literatures of RTA emitters featuring through space conjugation (TSC) of O or N atoms. Thus, the distances of which were obtained from their corresponding crystalline structures.

Name	Structure	CDCCID	Distance(Å)	Ref.
L-ser	HO NH ₂ OH	1142448	2.77 ± 0.07	[6]
L-lys	H ₂ N NH ₂ OH	1243851	2.84 ± 0.13	[6]
D+xylose	OH OH OH	1298199	2.75 ± 0.05	[7]
Cellulose	$\begin{bmatrix} 0H & HO & OH \\ 0 & 0H & 0H \\ HO & 0H & HO \end{bmatrix}_{n}$	792796	2.73 ± 0.20	[7]
L-Ile	он NH2	1142415	3.02 ± 0.29	[6]
D+glucose	HO OH OH OH OH	1169296	2.77 ± 0.05	[7]
Xylitol	он но он он он он	1298203	2.77 ± 0.08	[8]
Chitosan	$\begin{bmatrix} 0 \\ 0 \\ H \\ 0 \\ H \\ 0 \end{bmatrix}_{H_2} n$	1951228	2.84 ± 0.07	[7]
D+galactose	но он он он он	1101280	2.77 ± 0.10	[7]

For unconventional RTP-emissive clusteroluminogens, the distance of intermolecular N\O atoms should be a significant parameter for TSC. In principle, the TSC will be stronger as the distance decreased, however those species are hold by H bonds, so the resulted interval is actually located on H bond length (for intermolecular distance). Correspondingly, for intramolecular distance, the distance was mainly affected by covalent bond which has a relative certain value in a specific molecular.

S2.2 EDTA and its analogues-based carbon dots

Recently, great attempts have been made to construct carbon dots-based afterglow materials from EDTA and its analogues. Because of the diversity of their construction methodologies, matrices or construct self-protective structures, different afterglow characteristics would be produced.^[9] However, these carbon dots still share the following properties:

- (1) lifetime up to hundreds of milliseconds;
- (2) $\lambda_{ex-dependent}$ emission;
- (3) RTP emission wavelength around 500 nm.

Obviously, the above properties are similar to the RTP of EDTA and its analogues.

 Table S4.
 Summary of the room temperature phsoshporescence of carbon dots with EDTA

 and its analogues as precusors.

Carbon dots	precursors	$\lambda_{ m Phos}$	$ au_{Phos}$	Ref.
CDs-LDHs		320 ex: 505 nm 360 ex: 520 nm	~0.3 s	[10]
CDs-PVA	EDTA Disodium sait	325 ex: 500 nm	0.38 s	[11]
CD-APS1	HO _{NH2} Ethanolamine	360 ex: 500 nm	0.707 s	[12]

NCDs	HO HO OH OH OH OH OH OH HO HO NH ₂ OH NH ₂ OH OH OH OH OH OH OH OH OH OH OH OH OH	320 ex: 525 nm	0.747 s	[13]
P-CDs	$H_{2N} \xrightarrow{NH_2} H_0 \xrightarrow{P}_{OH} H_0$ Ethylenediamine Phosphoric Acid	340 ex: 538 nm	340 ex: 1.39 s	[14]
URTP CDs	HO NH ₂ Ethanolamine Phosphoric Acid	320 ex: 530 nm 340 ex: 545 nm 400 ex: 570 nm	340 ex: 1.46 s	[15]
FCNDs	HO HO HO HO HO HF HF HF HF HF HF HF HF HF HF HF HF HF	280 ex: 455 nm 360 ex: 500 nm	340 ex: >1 s	[16]
PCDsI-1	H ₂ N NH ₂ Ethylenediamine	365 ex: 494 nm	0.658 s	[17]
CD-1@PVA	HO HO OH OH Citric Acid	402 ex: 535 nm	>0.1 s	[18]
CDs	$\begin{bmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}^{2} \cdot Na^{*} Na^{*}$ $HO + O + O = 0$ $H_{2}N + NH_{2}$ EDTA Disodium salt urea	321 ex: 529 nm	0.269 s	[19]
a-CDs/BA	HO HO Citric Acid	350 ex: 515 nm 380 ex: 540 nm 420 ex: 565 nm	350 ex: 1.6 s	[20]
P-CDs	он но он но он он он Triethanolamine Phosphoric Acid	356 ex: 518 nm	0.821 s	[21]
AA-CDs	HO NH ₂ L-aspartic Acid	300 ex: 580 nm 365 ex: 610 nm 450 ex: 650 nm	312 ex: 0.241 s	[22]
CDs@SiO2	Rice husks	260 ex: 464 nm	5.72 s	[23]
CDs	HO HO O O HO H ₂ N NH ₂ NH ₂ Succinic Acid Diethylenetriamine	254 ex: 500 nm 365 ex: 530 nm 420 ex: 570 nm	312 ex: 0.880 s	[24]
NCDs	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	365 ex: 519 nm	0.459 s	[25]
CD-5.0	H ₂ N Urea	365 ex: 581 nm	0.335 s	[26]
NCD1	$H_{2N} H_{N} H_{$	254 ex: 430 nm 365 ex: 500 nm	254 ex: 1.11 s 365 ex: 0.53 s	[27]

Section S3. EDTA

S3.1 Confirmation of the RTP from EDTA

Processes for the Manufacturing of EDTA

(1) Dominant method
$H_2NCH_2CH_2NH_2 + 4NaCN + 4HCHO + 4H_2O \rightarrow (CH_2COONa)_2NCH_2CH_2N(CH_2COONa)_2 + 4NH_3 \uparrow$
$(CH_2COONa)_2NCH_2CH_2N(CH_2COONa)_2 + 2H_2SO4 \rightarrow (CH_2COOH)_2NCH_2CH_2N(CH_2COOH)_2 + 2Na_2SO_4)$
Possible byproducts: NH _{3,} Na ₂ SO4
(2) Subsidiary method
$H_2NCH_2CH_2NH_2 + 4HCN + 4HCHO \rightarrow (CH_2CN)_2NCH_2CH_2N (CH_2CN)_2 + 4H_2O$
$(CH_2CN)_2NCH_2CH_2N (CH_2CN)_2 + 8H_2O + 4HCI \rightarrow (CH_2COOH)_2NCH_2CH_2N(CH_2COOH)_2 + 4NH_4CI \rightarrow (CH_2COOH)_2NCH_2N(CH_2COOH)_2 + 4NH_4CI \rightarrow (CH_2COOH)_2 + 4NH$
Possible byproducts: NH ₄ CI
(3) Rarely used method
2CICH₂COOH + Na ₂ CO ₃ \rightarrow 2CICH ₂ COONa + CO ₂ \uparrow + H ₂ O
$4CICH_2COONa + \mathbf{H_2NCH}_2CH_2NH_2 + 4NaOH \rightarrow (CH_2COONa)_2NCH_2CH_2N(CH_2COONa)_2 + 4NaCI + NaCI + N$
4H ₂ O
$(CH_2COONa)_2NCH_2CH_2N(CH_2COONa)_2 + 2H_2SO_4 \rightarrow (CH_2COOH)_2NCH_2CH_2N(CH_2COOH)_2 + 2Na_2SO_4 \rightarrow (CH_2COOH)_2NCH_2OOH)_2 + 2Na_2SO_4 \rightarrow (CH_2COOH)_2 + 2NA_2 \rightarrow (CH_2COOH)_2 + 2NA_2 \rightarrow (CH_2COOH)_2 + 2NA_2 \rightarrow (CH_2COOH)_$
Possible byproducts: HOCH ₂ COOH, Na ₂ SO ₄ , NaCl

Figure S1. General processes for producing of EDTA.

Manufacture	Purity	$\lambda_{\rm ex} = 280 \ \rm nm$		$\lambda_{\rm ex} = 360 \ {\rm nm}$	
		$\lambda_{em, P} / nm$	τ_P / s	$\lambda_{em,P}/nm$	$ au_P \ / \ s$
Aladdin	99.99%	476	0.228	537	0.181
General	000/	176	0.217	540	0.122
Reagent	9970	470	0.217	540	0.132
Adamas Beta	99%	472	0.205	538	0.137
SCRC	99%	478	0.164	541	0.186
Alfa Aesar	99.4%	462	0.376	535	0.256

Table S5. Summary of the emission properties of EDTA from different manufactories.



Figure S2. The phosphorescence spectrum of EDTA dispersed in PMMA and blank PMMA film (delay = 10 ms, λ_{ex} = 280 nm). The film was prepared by dissolving PMMA and EDTA into DCM solvent, then spread on clean quartz slide.



Figure S3. The excitation-dependent phosphorescence emission spectra (delay time: 10 ms) and phosphorescence lifetime of EDTA from different manufactories.



Figure S4. Phosphorescence spectra (A, delay time: 10 ms) and lifetime (B) of NaCl and blank quartz (as controls).

S3.2 Temperature and excitation dependency of phosphorescence from EDTA



Figure S5. Temperature dependent phosphorescence emission of EDTA (delay = 10 ms, λ_{ex} = 360 nm).



Figure S6. The excitation-dependent phosphorescence emission spectra (A, delay = 20 ms) and phosphorescence lifetime (B) of EDTA at 77 K.

S3.3 Crystalline structure



Figure S7. Crystalline data of EDTA. Experimental XRD pattern of EDTA sample matches well with simulated one from EDTA single crystal data in Cambridge Structural Database (https://www.ccdc.cam.ac.uk/) (ID: 1148827).



Figure S8. The excitation-dependent phosphorescence emission spectra (A, delay = 20 ms) (delay = 10 ms) of EDTA crystal and grinded powder under room temperature.

S3.4 Theoretical calculations

Hole & Electron Distribution				
<i>f</i> = 0.019		EDTA		
	Related molecular of	orbitals in Excitation		
Occ	upied	Un	occupied	
MO 76 (38%)	MO 77 (51%)	MO 78 (26%)	MO 79 (25%)	

Figure S9. The TD-DFT calculation of EDTA monomer. Real space representation of hole and electron distributions (isovalue = 0.0008) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron. From the results above, the excitation was ascribed to the lone pair electrons of N/O atoms.

Section S4. EDTA Salts



S4.1 Phosphorescence properties

Figure S10. The emission property of EDTA-Na₂: (A) the $\lambda_{ex-dependent}$ phosphorescence emission spectra (delay = 10 ms); (B) phosphorescence lifetime.



Figure S11. The excitation-dependent phosphorescence emission spectra (delay = 10 ms) and phosphorescence lifetime of EDTA-Na₂ from different manufactories.

Manufacture	Purity	$\lambda_{\rm ex} = 280 \ \rm nm$		$\lambda_{\rm ex} = 360 \ \rm nm$	
		$\lambda_{em, P} / nm$	$ au_{P} \ / \ s$	$\lambda_{em, P} / nm$	$ au_{P}$ / s
Aladdin	99.99%	475	0.224	517	0.160
General	99%	466	0.205	523	0.149
Reagent					
Solarbio	99.9%	463	0.272	520	0.174
Sigma	99%	475	0.199	517	0.176

Table S6. Summary of the emission properties of EDTA-Na2 from different manufactories.

Figure S12. The $\lambda_{ex-dependent}$ phosphorescence emission spectra (A, delay = 20 ms) and phosphorescence lifetime (B) of EDTA-Na₂ at 77 K.

Figure S13. The excitation-dependent phosphorescence emission spectra (A, delay = 10 ms) and phosphorescence lifetime (B) of EDTA-Na₄ at room temperature.

Figure S14. The excitation-dependent phosphorescence emission spectra (A, delay = 10 ms) and phosphorescence lifetime (B) of EDTA- Li_2 at room temperature.

Figure S15. The excitation-dependent phosphorescence emission spectra (A, delay = 10 ms) and phosphorescence lifetime (B) of EDTA- K_2 at room temperature.

Figure S16. The excitation-dependent phosphorescence emission spectra (A, delay = 10 ms) and phosphorescence lifetime (B) of EDTA- $(NH_4)_2$ at room temperature.

S4.2 Afterglow Images

Figure S17. Afterglow images of EDTA-Na₂.

Upper panel: photographs directly taking with a camera, excited with 280 nm UV light from the FL-3 spectrofluorometer;

Bottom panel: photographs directly taking with a camera, excited with 365 nm UV light from the FL-3 spectrofluorometer.

S4.3 Crystalline structure

Crystallographic data for EDTA-Na ₂ crystal							
Empirical formula	C ₁₀ H ₂₀ N ₂ Na ₂ O ₁₀	$\rho_{calc}g/cm^3$	1.752				
Formula weight	374.26	µ/mm⁻¹	0.204				
Temperature/K	293(2)	F(000)	784				
Crystal system	Orthorhombic	Radiation	ΜοΚα (λ = 0.71073)				
Space group	Pbca	2θ range for data collection/^	6.548 to 58.302				
a/Â	9.9072(6)	Index ranges	$-8 \le h \le 13$, $-11 \le k \le 11$, $-21 \le l \le 13$				
b/Â	8.9556(5)	Reflections collected	3871				
c/Â	15.9942(11)	Independent reflections	1636 [R_{int} = 0.0288, R_{sigma} = 0.0475]				
α/°	90	Data/restraints/parameters	1636/2/125				
β/°	90	Goodness-of-fit on F ²	1.032				
γ/°	90	Final R indexes [I>=2σ (I)]	R ₁ = 0.0420, wR ₂ = 0.0925				
Volume/Å ³	1419.08(15)	Final R indexes [all data]	R ₁ = 0.0710, wR ₂ = 0.1036				
Z	4	Largest diff. peak/hole / e Å $^{-3}$	0.28/-0.23				

Figure S18. Single-crystal structure with probability ellipsoid of EDTA-Na₂ at the 50 % level. EDTA-Na₂ single crystal was prepared by placing its solution and EtOH together and sealed under room temperature. The crystal data was uploaded into CCDC (ID: 2051489).

Figure S19. The RTP property of EDTA-Na₂ (delay = 10 ms) after removal of the crystalline water.

Figure S20. The excitation-dependent phosphorescence emission spectra (A, delay = 10 ms) of EDTA-Na₂ crystal and grinded powder under room temperature.

S4.4 Theoretical calculations

Hole & Electron Distribution						
<i>f</i> = 0.024		EDTA-Na ₂				
Related molecular orbitals in Excitation						
Occ	upied	Un	occupied			
	Rik Stor					
MO 76 (12%)	MO 77 (78%)	MO 78 (9.6%)	MO 79 (75%)			

Figure S21. The TD-DFT calculation of EDTA²⁺. Real space representation of hole and electron distributions (isovalue = 0.0003) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02~0.03). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron. From the results above, the excitation was ascribed to the lone pair electrons of N/O atoms.

Figure S22. The energy diagram and SOC value between excited states of EDTA²⁺. ISC process from S_1 to T_2 state was thought to be most possible.

S5.1 Phosphorescence properties

Figure S23. The emission property of EDTA-Na₂-Mg (delay = 10 ms) under room temperature.

Figure S24. The emission property of EDTA-Na₂-Ca (delay = 10 ms) under room temperature.

Figure S25. The emission property of EDTA-Na₂-Sr (delay = 10 ms) under room temperature.

Figure S26. The emission property of EDTA-2Na-Ba (delay = 10 ms) under room temperature.

Figure S27. Heavy atom effect. For EDTA chelates with different metal ions, heavier chelate possesses stronger phosphorescence intensity and shorter lifetime which was ascribed to the Heavy atom effect (delay = 10 ms).

EDTA-Na ₂ -2H ₂ O					EDTA-NaCa
Stirring $ riangle$	Evaporate Recrystallization	Filtration	Drying 70°C	Grinding 1 min	ED 17-1102-00
EDTA-Na ₂ -2H ₂ O					EDTA-Na -Sr
Stirring $ riangle$	Evaporate Recrystallization	Filtration	Drying 70°C	Grinding 1 min	
EDTA-Na ₂ -2H ₂ O					
Stirring △	Evaporate Recrystallization	Filtration	Drying 70°C	Grinding 1 min	
	$\begin{tabular}{c} EDTA-Na_2-2H_2O\\ \hline Stirring \triangle\\ \hline EDTA-Na_2-2H_2O\\ \hline Stirring \triangle\\ \hline EDTA-Na_2-2H_2O\\ \hline Stirring \triangle\\ \hline \end{tabular}$	EDTA-Na2-2H2OStirring \triangle Evaporate RecrystallizationEDTA-Na2-2H2OEvaporate RecrystallizationStirring \triangle Evaporate RecrystallizationEDTA-Na2-2H2OEvaporate RecrystallizationStirring \triangle Evaporate Recrystallization	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Figure S28. Preparation of EDTA chelates.

EDTA metal chelates (Ca, Sr, Ba) were freshly prepared through procedures above. The reactive ratio was controlled in 1: 1, the phosphorescence of raw material EDTA-Na₂ has little effect according to large chelating reaction constant. Furthermore, the phosphorescence lifetime of products was obviously different from raw material. To eliminate the possible interferences of reaction temperature and morphology differences, the reactions were adopted under same condition, products were grinded to fine powder in 1 min. However, MgCl₂ will easily transfer to insoluble precipitate under same condition which can ascribed to the hydrolysis of Mg²⁺. Thus, commercial EDTA-Na₂-Mg was choosing which is also treated with grinding.

S5.2 Afterglow Images

EDTA-Na ₂ -Mg Ex = 280 nm		UV OFF 0.5 s	1 s	1.5 s	2.0 s	2.5 s	3 s	77 K 3.5 s
	UV ON	UV OFF						77 K
Ex = 365 nm		0.5 s	1 s	1.5 s	2.0 s	2.5 s	3 s	3.5 s

Figure S29. Afterglow images of EDTA-Na₂-Mg.

Upper panel: photographs directly taking with a camera, excited with 280 nm UV light from the FL-3 spectrofluorometer;

Bottom panel: photographs directly taking with a camera, excited with 365 nm UV light from the FL-3 spectrofluorometer.

	UV ON	UV OFF						77 K
EDTA-Na ₂ -Ca		0.5 s	1 s	1.5 s	2.0 s	2.5 s	3 s	3.5 s
Ex = 280 nm	(2)							
	UV ON	UV OFF						77 K
Ex = 365 nm		UV OFF 0.5 s	1 s	1.5 s	2.0 s	2.5 s	3 s	<mark>77 К</mark> 3.5 s

Figure S30. Afterglow images of EDTA-Na₂-Ca.

Upper panel: photographs directly taking with a camera, excited with 280 nm UV light from the FL-3 spectrofluorometer;

Bottom panel: photographs directly taking with a camera, excited with 365 nm UV light from the FL-3 spectrofluorometer.

EDTA-Na ₂ -Sr Ex = 280 nm		UV OFF 0.5 s	1 s	1.5 s	2.0 s	2.5 s	3 s	77 K 3.5 s
	UV ON	UV OFF						77 K
Ex = 365 nm		0.5 s	1 s	1.5 s	2.0 s	2.5 s	3 s	3.5 s

Figure S31. Afterglow images of EDTA-Na₂-Sr.

Upper panel: photographs directly taking with a camera, excited with 280 nm UV light from the FL-3 spectrofluorometer;

Bottom panel: photographs directly taking with a camera, excited with 365 nm UV light from the FL-3 spectrofluorometer.

Figure S32. Afterglow images of EDTA-Na₂-Ba.

Upper panel: photographs directly taking with a camera, excited with 280 nm UV light from the FL-3 spectrofluorometer;

Bottom panel: photographs directly taking with a camera, excited with 365 nm UV light from the FL-3 spectrofluorometer.

S5.3 Theoretical calculations

Hole & Electron Distribution						
<i>f</i> = 0.048		EDTA-Na ₂ -Mg				
	Related molecular orbitals in Excitation					
Occ	upied	Un	occupied			
			entite o			
MO 80 (5.9%)	MO 81 (79%)	MO 83 (85%)	MO 84 (4.7%)			

Figure S33. The TD-DFT calculation of EDTA-Na₂-Mg. Real space representation of hole and electron distributions (isovalue = 0.0008) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02~0.022). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron. From the results above, the excitation was ascribed to the lone pair electrons in EDTA chelator.

Figure S34. The TD-DFT calculation of EDTA-Na₂-Ca. Real space representation of hole and electron distributions (isovalue = 0.0005) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = $0.02\sim0.03$). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron. From the results above, the excitation was ascribed to the lone pair electrons in EDTA chelator.

Figure S35. The TD-DFT calculation of EDTA-Na₂-Sr. Real space representation of hole and electron distributions (isovalue = 0.0005) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = $0.02\sim0.03$). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron. From the results above, the excitation was ascribed to the lone pair electrons in EDTA chelator.

Figure S36. The TD-DFT calculation of EDTA-Na₂-Ba. Real space representation of hole and electron distributions (isovalue = 0.0005) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = $0.02\sim0.03$). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron. From the results above, the excitation was ascribed to the lone pair electrons in EDTA chelator.

Section S6. EDTA Analogs

S6.1 Phosphorescence properties

Figure S37. The emission property of EDTAD (delay = 10 ms) and the afterglow image. Photographs were taken after the cut-off of Xe lamp excitation (280 nm and 365 nm) under 77 K in cryogenic chamber.

Figure S38. The phosphorescence spectrum (delay = 10 ms) and lifetime Trigtycolamidic Acid (NTA) under room temperature.

Figure S39. The phosphorescence spectrum (delay = 10 ms) and lifetime Diethylenetriamine pentaacetic Acid (DTPA) under room temperature.

Figure S40. The phosphorescence spectrum (delay = 10 ms) and lifetime Citric acid (CA) under room temperature.

Figure S41. The phosphorescence spectrum (delay = 10 ms) and lifetime Tartaric acid (TA) under room temperature.

S6.2 Theoretical calculations

Figure S42. The TD-DFT calculation of EDTAD. Real space representation of hole and electron distributions (isovalue = 0.0005) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = $0.015\sim0.02$). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron.

Figure S43. The TD-DFT calculation of NTA. Real space representation of hole and electron distributions (isovalue = 0.001) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02~0.03). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron.

Figure S44. The TD-DFT calculation of DTPA. Real space representation of hole and electron distributions (isovalue = 0.0003) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron.

Figure S45. The TD-DFT calculation of TTHA. Real space representation of hole and electron distributions (isovalue = 0.0003) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron.

Figure S46. The TD-DFT calculation of CA. Real space representation of hole and electron distributions (isovalue = 0.001) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron.

Figure S47. The TD-DFT calculation of TA. Real space representation of hole and electron distributions (isovalue = 0.0005) and the heat map of atoms' contribution to hole and electron respectively. Related molecular orbitals involved in excitation was also presented (isovalue = 0.02). For occupied orbitals, n% represents the contribution to Hole, for Unoccupied orbitals, n% represents the contribution to Electron.

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