

Electronic supplementary information

Emissive supramolecular ionic crystal combining a red-NIR phosphorescent $[\text{Re}_6\text{Se}_8\text{CN}_6]^{4-}$ cluster anion and a blue fluorescent tetraphenylethene counter-cation

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1. Experimental techniques

Starting reagents and solvents were purchased from commercial suppliers and used without further purification.

Energy dispersion spectroscopy (EDS) was performed by the use of the Hitachi TM-3000 electron microscope equipped with the Bruker Nano EDS analyzer.

Elemental analysis were performed with a Thermo Fisher Flash EA1112 microanalyzer at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO).

A suitable crystal of **TPE-Re** for X-ray diffraction single crystal experiment was selected and mounted on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector [*], using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, multilayer monochromator) at $T = 150(2) \text{ K}$.

NMR experiments were realized on a Bruker Avance III 400 MHz NMR spectrometers. All peaks were referenced to the methyl signals of TMS at $\delta = 0 \text{ ppm}$.

UV-vis absorption spectra were recorded on a Horiba Jobin Yvon Duetta spectrophotometer. The absolute quantum yields were measured with a C9920-03 Hamamatsu system.

Lifetime measurements and TRPL mapping at 296 K were realized using a picosecond laser diode (Jobin Yvon deltadiode, 375 nm) and a Hamamatsu C10910-25 streak camera mounted with a slow single sweep unit. Signals were integrated on the whole emission decay. Fits were obtained using origin software and the goodness of fit judge by the reduced χ^2 value and residual plot shape. Emission spectra were recorded with an Ocean Optics QEPro CCD spectrometer

[*] Thanks to FEDER funds

2. Synthetic Procedure

((Z)-1,2-bis(4-bromophenyl)-1,2-diphenylethene)¹ (**1**) and Cs₄[Re₆Se₈(CN)₆] \cdot 3H₂O² were synthesized according to previously reported procedures.

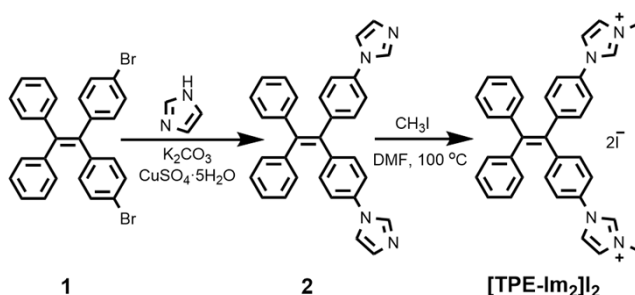


Figure S1. Scheme of the synthesis of [TPE-Im₂]²⁺I₂⁻

Synthesis of (Z)-1,2-bis(4-(1H-imidazol-1-yl)phenyl)-1,2-diphenylethene (**2**)

A 50 mL Schlenk flask was charged with **1** (900 mg, 1.9 mmol, 1 eq.), imidazole (2.53 g, 37 mmol, 20 eq.), K₂CO₃ (898 mg, 6.50 mmol, 3.5 eq.) and CuSO₄ \cdot 5H₂O (46 mg, 186 μ mol, 0.1 eq.). The solid mixture was then heated to 160 °C for 24 hours under an argon atmosphere. The reaction mixture was then cooled to rt and dissolved into distilled water. The remaining solid residue was extracted with methanol (150 mL) and the methanol solution was filtered through Celite. The filtrate was brought to dryness to give **2** (Yield: 99 %). ¹H NMR (400 MHz, DMSO-d₆): $\delta = 8.23$ (s, 2H), 7.72 (s, 2H), 7.48 (d, ³J = 8.5 Hz, 4H), 7.19 (d, ³J = 8.5 Hz, 4H), 7.11-7.15 (d, 5H), 7.03-7.07 (d, 5H), 7.08 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆): $\delta = 143.3, 142.1, 141.8, 138.9, 135.8, 135.6, 132.6, 131.1, 130.3, 128.5, 127.4, 119.9, 118.2$. HRMS (ASAP): [M+H]⁺ (C₃₂H₂₅N₄), m/z Calcd for: 465.2079, m/z Found: 465.2077.

Synthesis of (Z)-1,1'-((1,2-diphenylethene-1,2-diyl)bis(4,1-phenylene))bis(3-methyl-1H-imidazol-3-ium) iodide ([TPE-Im₂]²⁺I₂⁻)

2 (857 mg, 1.84 mmol, 1 eq.) and iodomethane (0.46 mL, 7.38 mmol, 4 eq.) were dissolved in 10 mL DMF and the reaction was heated to 100 °C for 24 hours. Then cooled to rt, washed with dichloromethane and dried in vacuo to give compound [TPEIm₂]²⁺I₂⁻ (Yield: 99 %). ¹H NMR (400 MHz, DMSO-d₆): $\delta = 9.73$ (s, 2H), 8.25 (s, 2H), 7.93 (s, 2H), 7.62 (d, ³J = 8.6 Hz, 4H), 7.29 (d, ³J = 8.6 Hz, 4H), 7.20 (t, ³J = 7.2 Hz, 6H), 7.08 (d, 4H), 3.92 (s, 6H). ¹³C NMR (101 MHz, DMSO-d₆): $\delta = 144.6, 143.8, 142.7, 137.8, 136.2, 133.4, 132.8, 131.0, 128.6, 127.7, 124.9, 121.5, 121.0, 36.6$. HRMS (ESI, MeOH/CH₂Cl₂, 9/1): M⁺ (C₃₄H₃₀N₄), m/z Calcd for: 247.12298 m/z Found: 247.1231.

Synthesis of [TPE-Im₂][Re₆Se₈(CN)₆] (TPE-Re)

75 mg (30 μ mol) of Cs₄[Re₆Se₈(CN)₆] \cdot 3H₂O (**Cs₄Re**) was dissolved in 5 ml of H₂O/methanol (1/1 v/v) mixture. 45 mg (61 μ mol) of [TPE-Im₂]²⁺I₂⁻ was dissolved in 5 ml of methanol. Resulting solutions were mixed with stirring which led to the formation of a yellow powder. The powder was collected, washed with water and methanol for 3 times and dry under vacuum at 60 °C for overnight (76 mg, 87%). The slow vapor diffusion of acetone into the solution of compound **TPE-Re** in DMSO led to the formation of single crystals suitable for X-Ray data collection. ¹H NMR (400 MHz, DMSO-d₆) $\delta = 9.69$ (s, 2H), 8.24 (t, $J = 1.9 \text{ Hz}$, 2H), 7.92 (t, $J = 1.8 \text{ Hz}$, 2H), 7.63 (d, $J = 8.3 \text{ Hz}$, 4H), 7.30 (d, $J = 8.2 \text{ Hz}$, 4H), 7.26 – 7.13 (m, 6H), 7.12 – 7.05 (m, 4H), 3.93 (s, 6H). EDS: Re:Se = 6.0:7.5 (no Cs and I were found). E.A.: calc. for C₇₄H₆₀N₁₄Re₆Se₈: C, 30.71; H, 2.09; N, 6.78; found: C, 30.19; H, 1.76; N, 6.61

3. NMR spectra

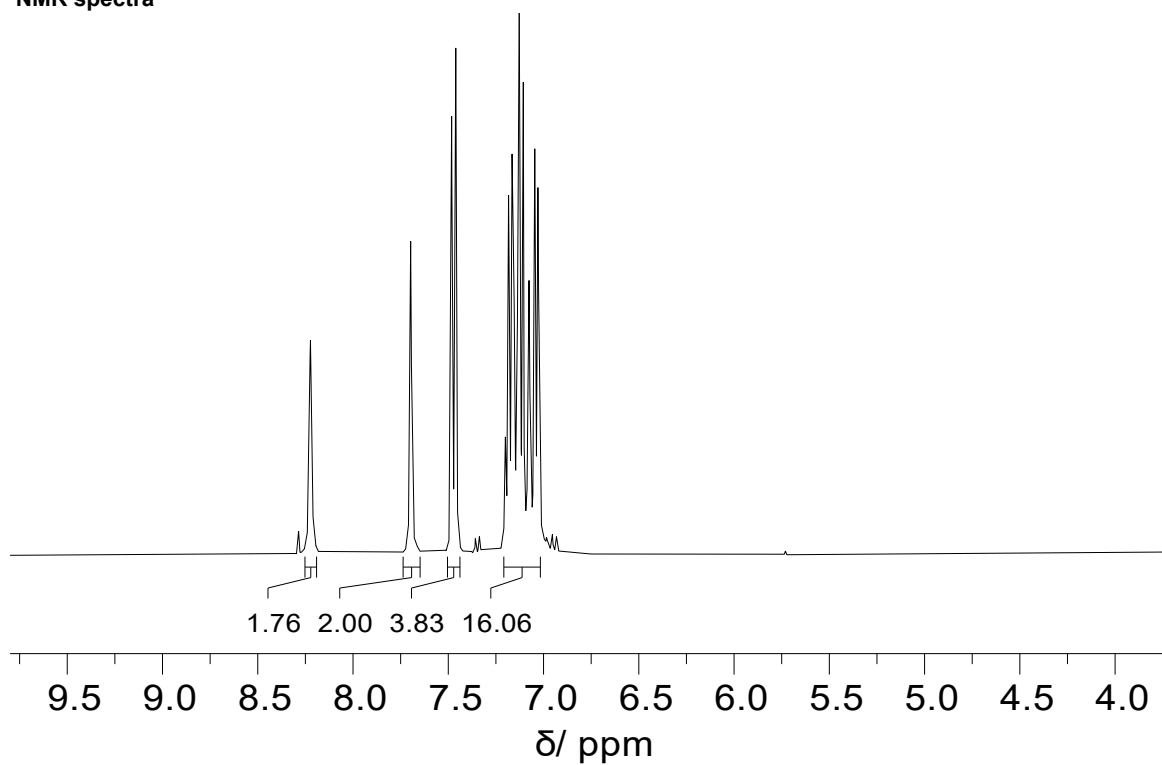


Figure S2. ^1H NMR (400 MHz, DMSO-d_6) spectrum of **2**

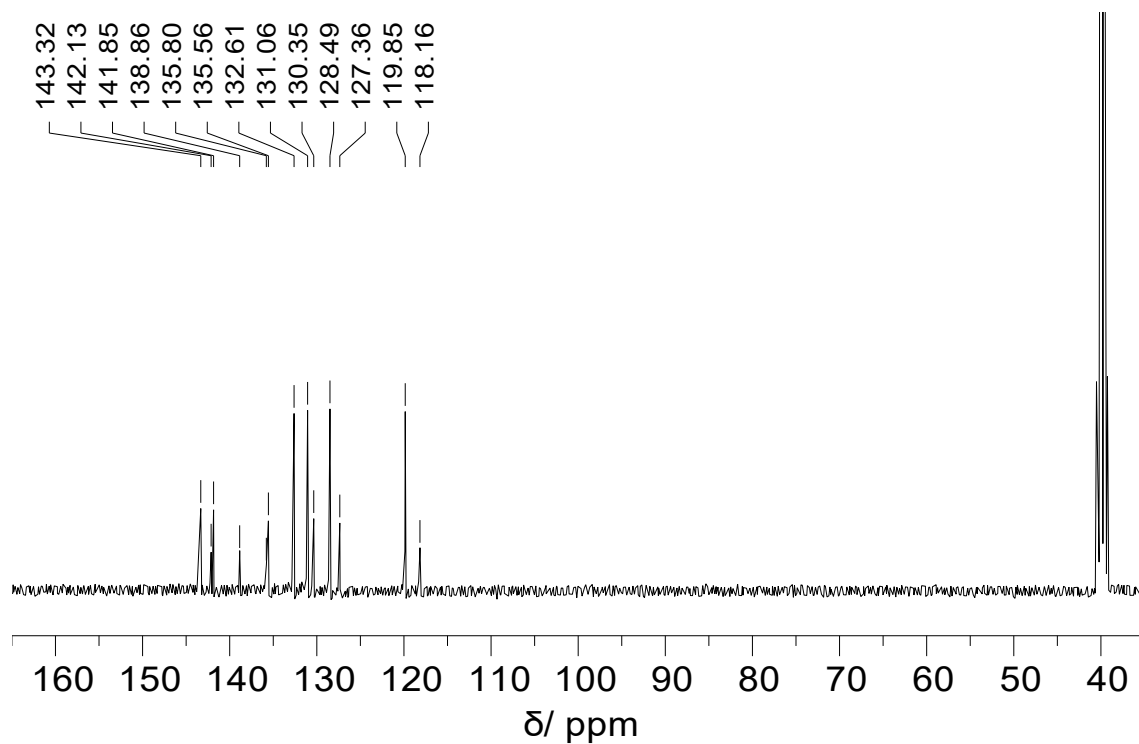


Figure S3. ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of **2**

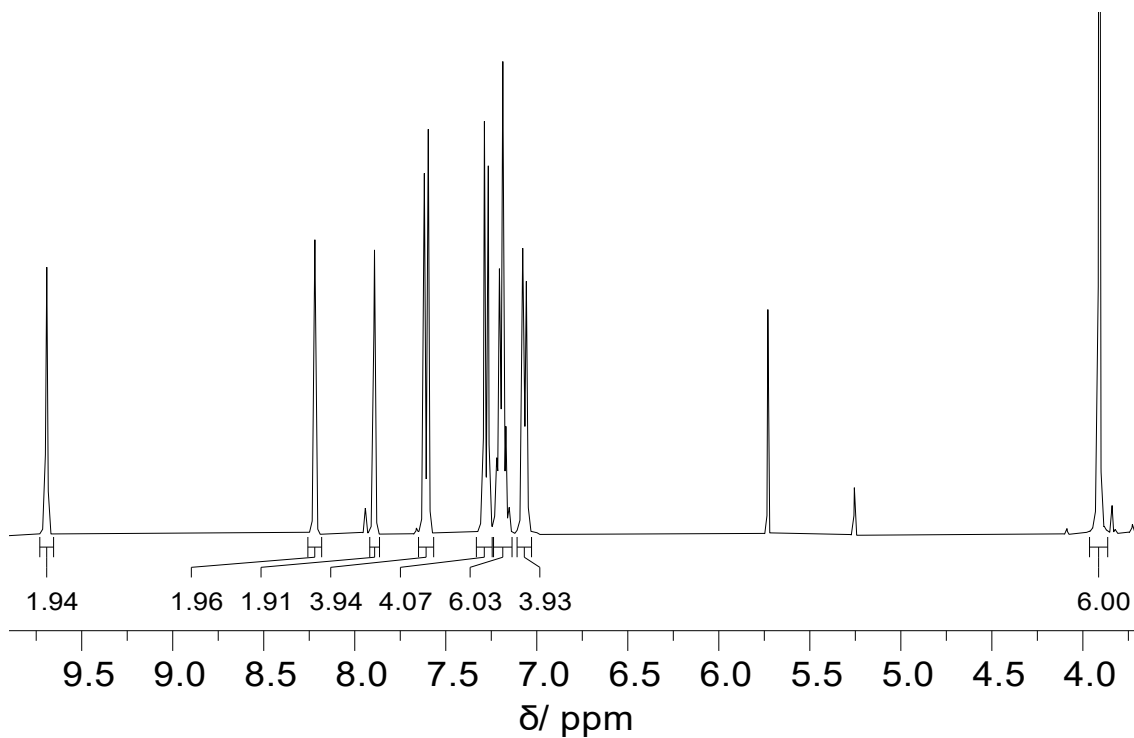


Figure S4. ^1H NMR (400 MHz, DMSO-d_6) spectrum of $[\text{TPEIm}_2]_2$

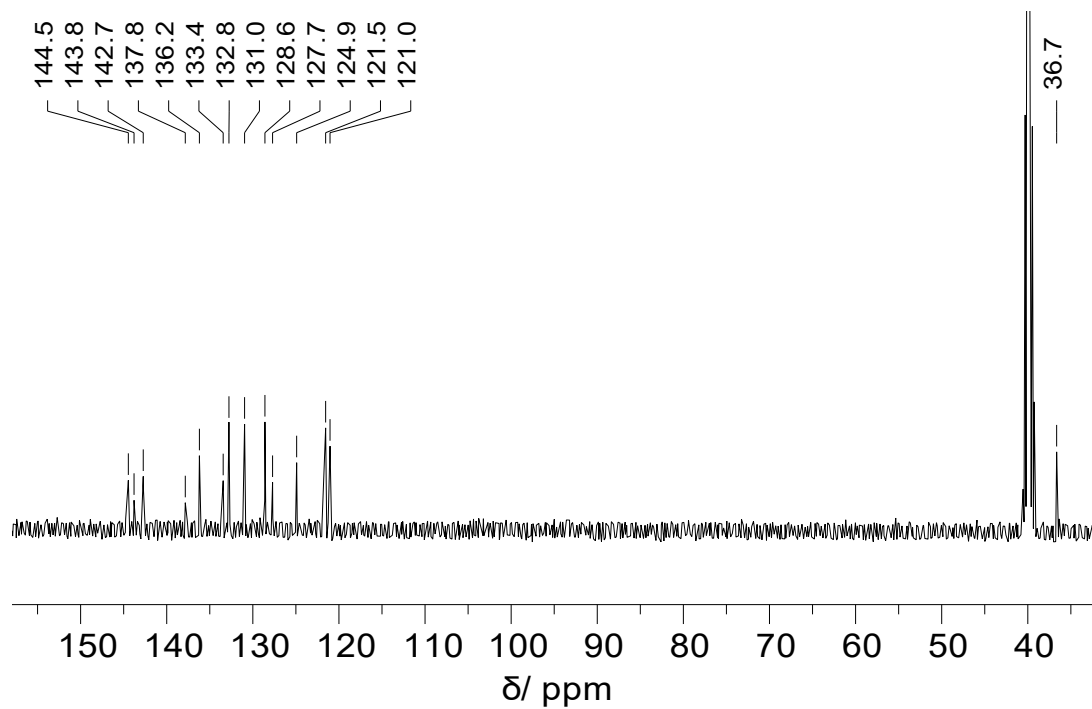


Figure S5. ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of $[\text{TPEIm}_2]_2$

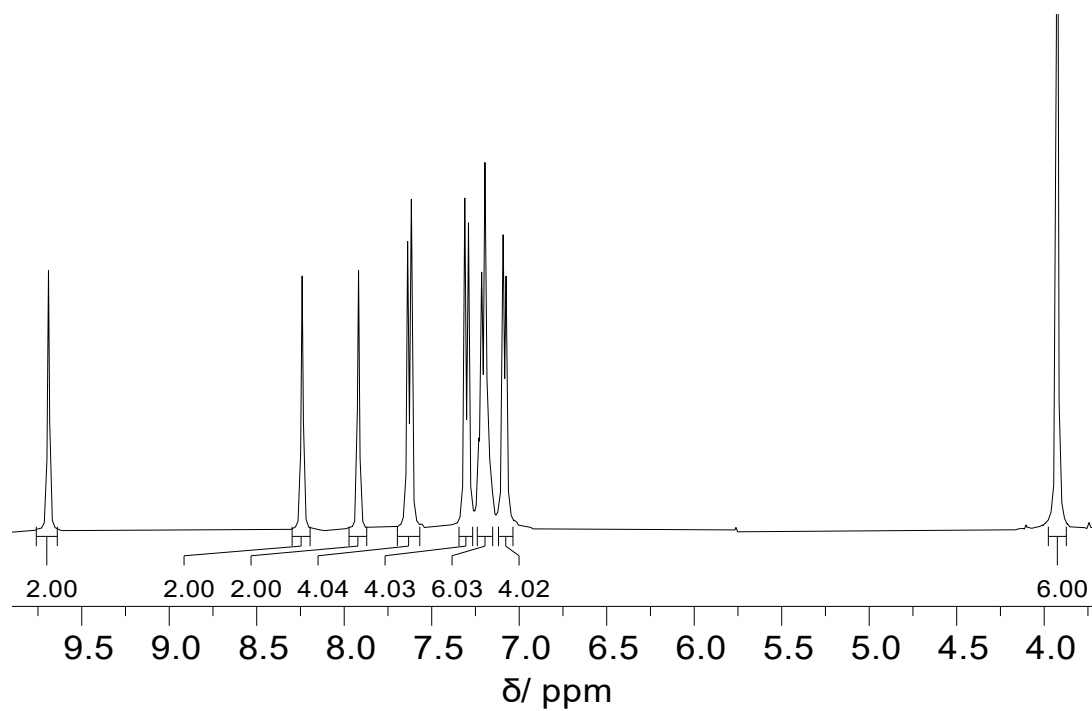


Figure S6. ^1H NMR (400 MHz, DMSO-d_6) spectrum of TPE-Re

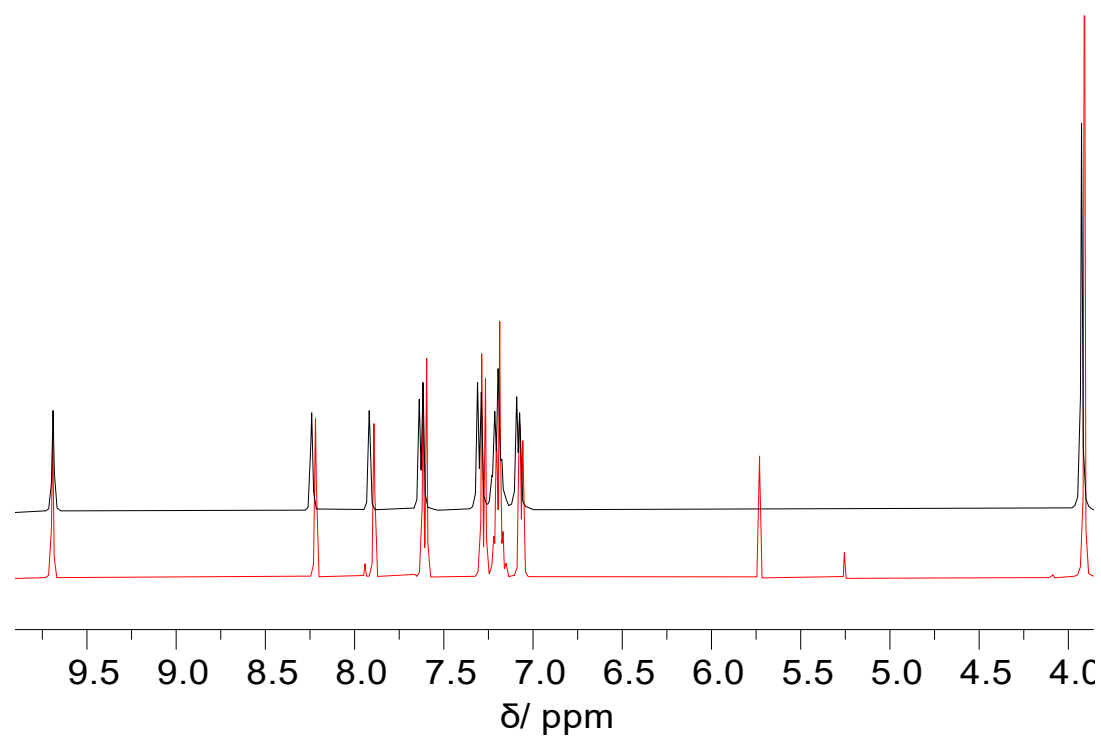


Figure S7. Comparison of ^1H NMR spectra in DMSO-d_6 of $[\text{TPE-Im}_2]_2$ (red line) and TPE-Re (black line)

4. Crystallographic data and structure refinement details

The crystal structure has been described in triclinic symmetry and P -1 (I.T.#2) centric space group (Rint = 0.0347). Cell parameters have been refined as follows: a = 13.3821(14), b = 14.4273(15), c = 16.1242(16) Å, α = 114.579(4), β = 94.841(4), γ = 102.837(4) °, V = 2704.8(5) Å³. Number of formula unit Z is equal to 2 and calculated density d and absorption coefficient μ values are 1.777 g·cm⁻³ and 9.415 mm⁻¹ respectively. Crystal structure was solved by dual-space algorithm using SHELXT program,³ and then refined with full-matrix least-squares methods based on F² (SHELXL⁴). The contribution of the disordered solvents to the calculated structure factors was estimated following the BYPASS algorithm,⁵ implemented as the SQUEEZE option in PLATON.⁶ A new data set, free of solvent contribution, was then used in the final refinement. All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. A final refinement on F² with 10269 unique intensities and 462 parameters converged at ωRF2 = 0.0949 (RF = 0.0389) for 7837 observed reflections with I > 2σ(I).

Table S1. Crystallographic Data and Structure Refinement Details for **TPE-Re**

Empirical formula	C ₃₇ H ₃₀ N ₇ Re ₃ Se ₄
Formula weight	1447.12 g/mol
Temperature	150(2) K
Radiation type	Mo-Kα
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P(-1) (I.T.#2)
	a = 13.3821(14) Å
	b = 14.4273(15) Å
	c = 16.1242(16) Å
Unit cell dimensions	α = 114.579(4)°
	β = 94.841(4)°
	γ = 102.837(4)°
Volume	2704.8(5) Å ³
Z, Calculated density	2, 1.777 g·cm ⁻³
Absorption coefficient	9.415 mm ⁻¹
F(000)	1324
Crystal size	0.350 x 0.150 x 0.100 mm
Crystal color	orange
Crystal description	plate
Diffractometer	D8 Venture (Bruker-AXS)
Detector	CMOS-PHOTON70
θ range for data collection	1.922 to 25.680°
(sinθ/λ) _{max} (Å ⁻¹)	0.610
h _{min} , h _{max}	-16, 16
k _{min} , k _{max}	-17, 17
l _{min} , l _{max}	-19, 19
Reflections collected / unique	36147 / 10269 [R(int) ^a = 0.0347]
Reflections [I > 2σ]	7837
Completeness to θ _{max}	0.998
Absorption correction type	multi-scan
Max. and min. transmission	0.390, 0.201
Refinement method	Full-matrix least-squares on F ²
H-atom treatment	H-atom parameters constrained
Data / restraints / parameters	10269 / 30 / 462
^b S (Goodness-of-fit)	1.050
Shelxl weighting scheme parameters	a = 0.0408, b = 30.092
Final R indices [I > 2σ]	R1 ^c = 0.0389, wR2 ^d = 0.0949
R indices (all data)	R1 ^c = 0.0560, wR2 ^d = 0.1080
Δρ _{max} , Δρ _{min}	2.339, -1.583 e ⁻ ·Å ⁻³

$${}^a R_{int} = \sum |F_0^2 - \langle F_0^2 \rangle| / \sum [F_0^2]$$

$${}^b S = \left\{ \sum [w(F_0^2 - F_c^2)^2] / (n - p) \right\}^{1/2}$$

$${}^c R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$$

$${}^d wR_2 = \left\{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \right\}^{1/2}$$

$$w = 1 / [\sigma(F_0^2) + aP^2 + bP] \text{ where } P = [2F_c^2 + MAX(F_0^2, 0)] / 3$$

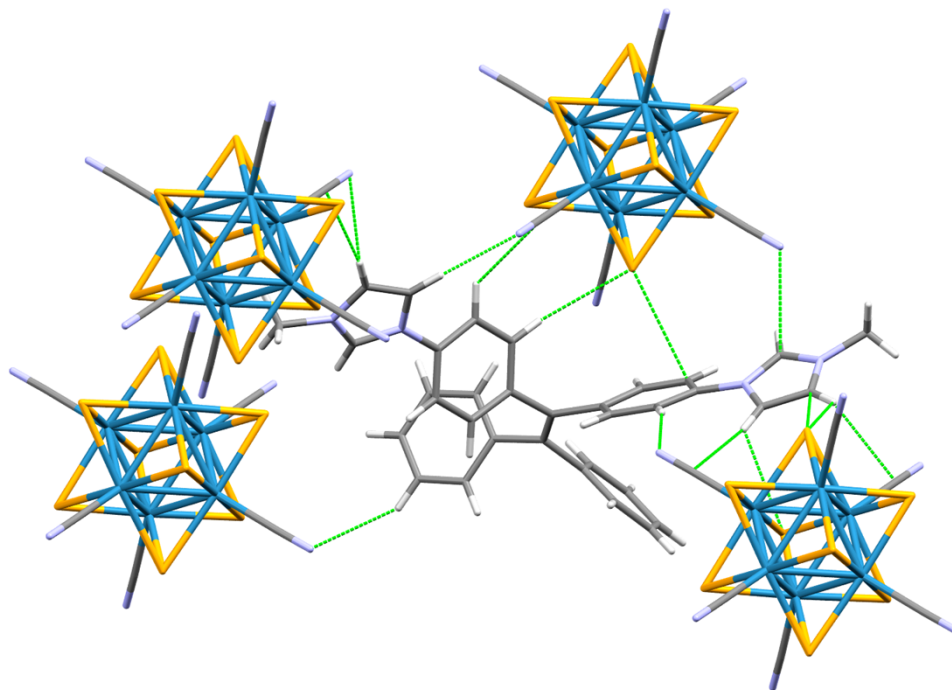


Figure S8. Representation of short contacts (green) between TPE dication and four cluster units in **TPE-Re**; distances vary from 2.5 to 3.6 Å

5. Emission decay profiles

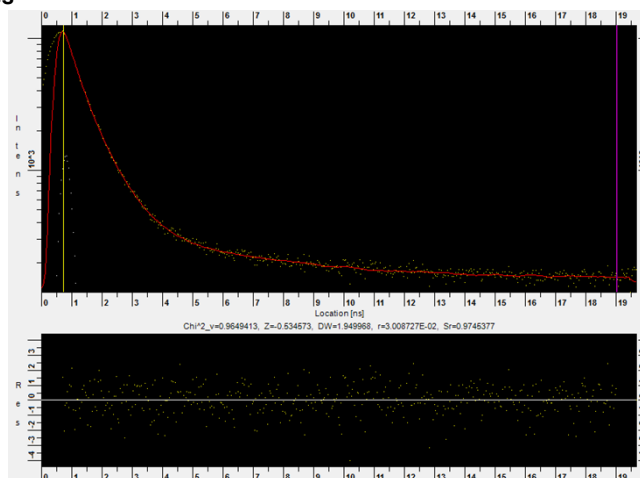


Figure S9. Emission decay profile ($\lambda_{\text{ex}} = 375 \text{ nm}$) of solid **[TPE-Im₂]₂**

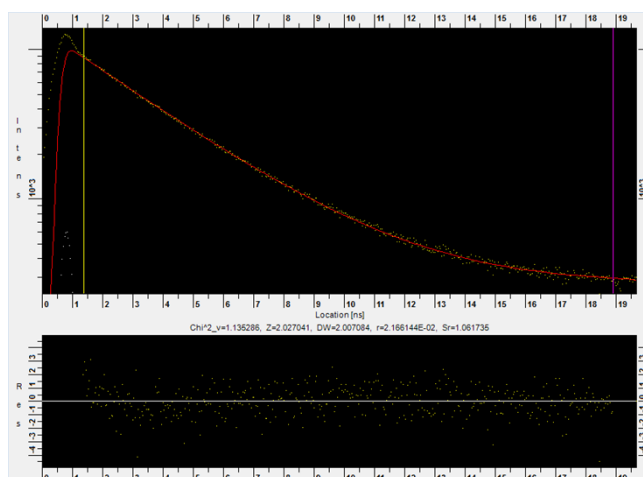


Figure S10. Emission decay profile ($\lambda_{\text{ex}} = 375 \text{ nm}$) of TPE-Re in deaerated DMSO focused on TPE component

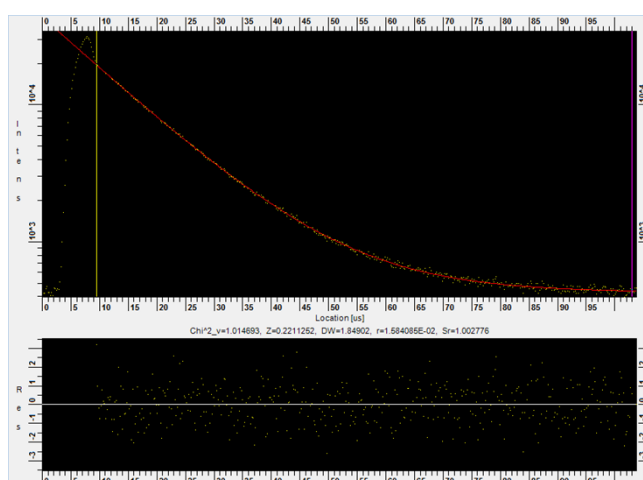


Figure S11. Emission decay profile ($\lambda_{\text{ex}} = 375 \text{ nm}$) of TPE-Re in deaerated DMSO focused on Re component

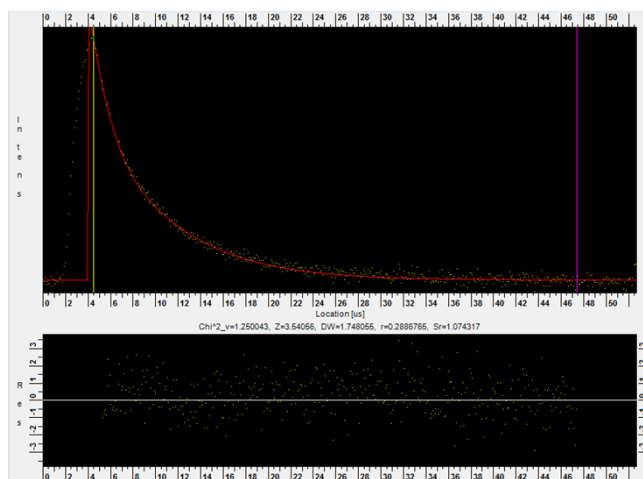


Figure S12. Emission decay profile ($\lambda_{\text{ex}} = 375 \text{ nm}$) of solid TPE-Re

6. Forster radius

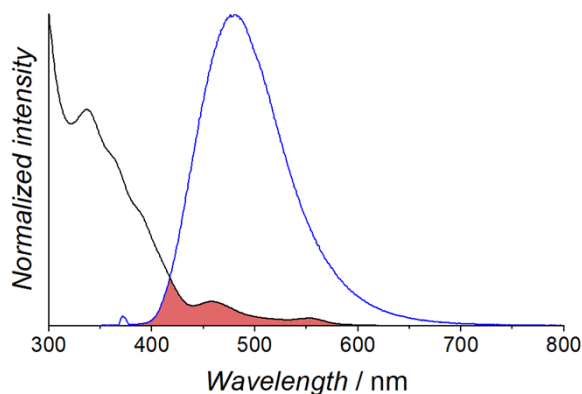


Figure S13. Representation of crossing of absorption spectrum of Cs_4Re in H_2O and emission spectrum of $[\text{TPE-Im}_2]_2$ in the solid state

The following Forster rate equation describes the energy transfer by dipolar interaction:

$$k = \frac{1}{\tau_D} \left(\frac{R_0}{r} \right)^6, R_0^6 = 8.785 \times 10^{-5} \frac{K^2 \Phi_D J}{n^4}$$

Where τ_D is the donor lifetime in the absence of acceptor, r is the donor-acceptor distance, and R_0 is the Förster distance at which the energy transfer rate is equal to the decay rate. The Förster distance is related to the orientation factor, K^2 between donor and acceptor, and the donor and acceptor spectroscopic properties. K was taken as $2/3$ that is appropriate for dynamic random orientation averaging of the donor and acceptor. Φ_D is the quantum yield of the donor in the absence of an acceptor (0.06 for $[\text{TPE-Im}_2]_2$). The index of refraction, n , is the index of refraction of DMSO: 1.4793. J is the overlap integral between the donor and acceptor that is calculated using the following equation:

$$J = \int_0^{\infty} F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$

Where F_D is the area-normalized fluorescence spectrum of the donor,⁷ ε_A is the molar absorption coefficient of the acceptor. The scaling constant is set such that when ε is in units of $\text{M}^{-1}\text{cm}^{-1}$ and wavelength in units of nm, the Förster distance is in units of Å.⁸

The Förster radius was evaluated at 298K.

7. Excitation spectra

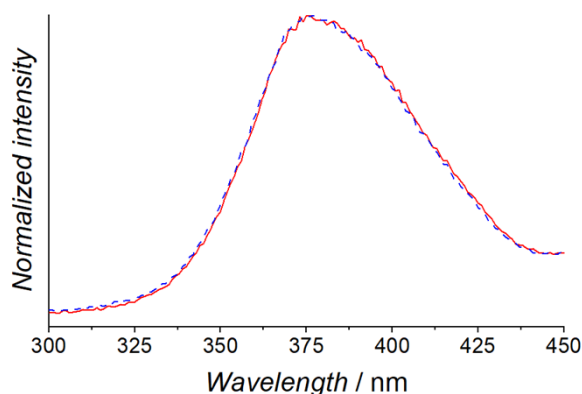


Figure S14. Excitation spectra of TPE-Re in deaerated DMSO for $\lambda_{em} = 440$ nm (blue dashed line) and $\lambda_{em} = 710$ nm (red solid line)

8. Absorption spectrum of TPE-Re

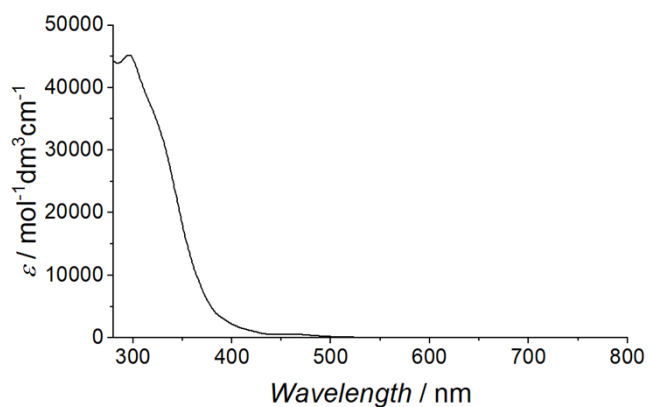


Figure S15. Absorption spectrum of TPE-Re in DMSO

1. X. Zhou, H. Li, Z. Chi, X. Zhang, J. Zhang, B. Xu, Y. Zhang, S. Liu and J. Xu, *New Journal of Chemistry*, 2012, **36**, 685-693.
2. A. Ledneva, S. Ferlay, N. G. Naumov, M. Mauro, S. Cordier, N. Kyritsakas and M. W. Hosseini, *New Journal of Chemistry*, 2018, **42**, 11888-11895.
3. G. Sheldrick, *Acta Cryst. Section A*, 2015, **71**, 3-8.
4. G. Sheldrick, *Acta Cryst. C-Cryst. Struct. Commun.*, 2015, **71**, 3-8.
5. P. Vandersluis and A. L. Spek, *Acta Cryst. A*, 1990, **46**, 194-201.
6. A. I. Spek, *Acta Crystallogr. C Struct Chem*, 2015, **71**, 9-18.
7. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy, third edition*, Springer, Boston, MA, 2006.
8. P. G. Wu and L. Brand, *Anal. Biochem.*, 1994, **218**, 1-13.