

Supporting Information for:

Homoleptic lanthanide complexes containing a redox-active ligand and the investigation of their electronic and photophysical properties

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X-ray crystallography:

From complex **4** data were collected on a Bruker Kappa APEX-DUO diffractometer using monochromated Mo-K α radiation and were measured using a combination of ϕ scans and ω scans. The data were processed using APEX2 and SAINT (Bruker, 2007). Absorption corrections were carried out using SADABS (Bruker, 2007). The structure was solved using SHELXT (Sheldrick, 2015a) and refined using SHELXL (Sheldrick, 2015b) for full-matrix least-squares refinement that was based on F^2 . All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom. During the refinement of the structure, electron density peaks were located that were believed to be highly disordered solvent molecules (possibly CHCl₃/CH₃CN based on the crystallization solvents). Attempts made to model the solvent molecule were not successful. The SQUEEZE (Spek, 2015) option in PLATON (Spek, 2009) indicated there was a large solvent cavity of 156 Å³. In the final cycles of refinement, this contribution of 65 electrons to the electron density was removed from the observed data. The density, the $F(000)$ value, the molecular weight and the formula are given without taking into account the results obtained with the SQUEEZE (Spek, 2015) option in PLATON (Spek, 2009).

References

Bruker (2007). APEX2, SAINT & SADABS Bruker AXS Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (2015a). Acta Cryst. A71, 3–8.

Sheldrick, G. M. (2015b). Acta Cryst. C71, 3–8.

Spek, A. L. (2009). Acta Cryst. D65, 148–155.

Spek, A. L. (2015). Acta Cryst. C71, 9–18.

Brock MS Facility - Bruker HCT Ultra - LCMS

Analysis Info

Analysis Name D:\Data\16Feb\MLH0137.d
Method QL 160105.m
Sample Name ~~MLH0137.d~~
Comment

Acquisition Date 10/02/2016 8:11:17 PM

Operator LIQUN QIU
Instrument HCTultra

Acquisition Parameters

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
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Accumulation Time	26280 μ s	Averages	5 Spectra	Auto MS/MS	off

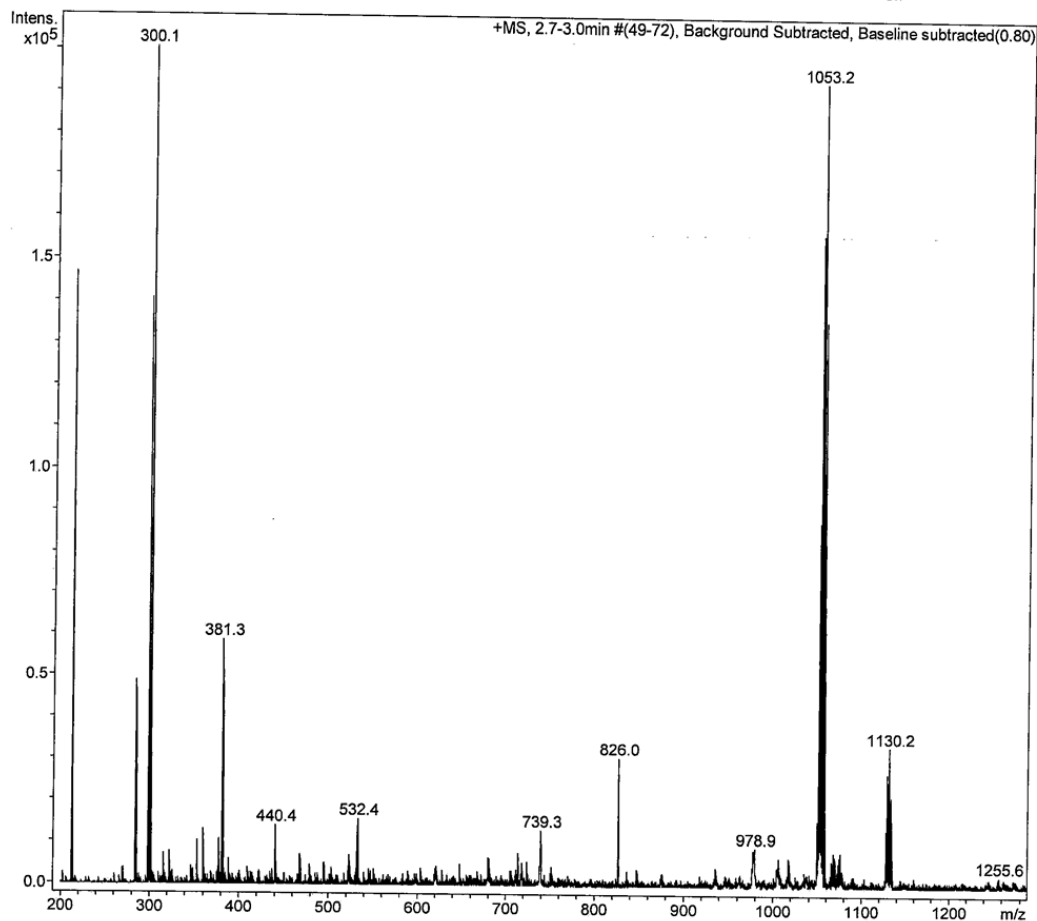


Figure S1. ESI mass spectrum (positive ion mode) of **1**.

Brock MS Facility - Bruker HCT Ultra - LCMS

Analysis Info

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 Sample Name RT-1-123
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Acquisition Date 10/02/2016 8:11:17 PM

Operator LIQUN QIU
 Instrument HCTultra

Acquisition Parameters

Ion Source Type ESI
 Mass Range Mode Std/Enhanced
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 Accumulation Time 26280 μ s

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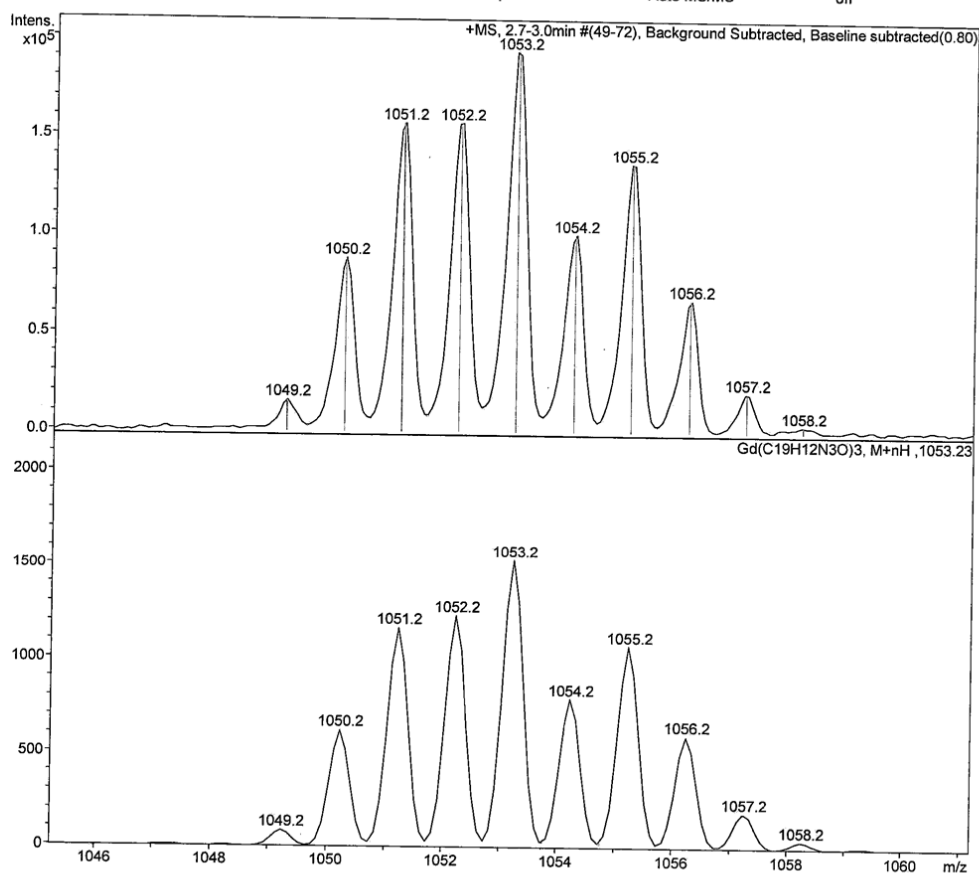


Figure S2. Experimental (top) and theoretical (bottom) isotopic distribution for $[M+H]^+$ peak for

1.

Brock MS Facility - Bruker HCT Ultra - LCMS

Analysis Info

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Method QL 160105.m
Sample Name ~~RT 2.145~~
Comment

Acquisition Date 10/02/2016 7:07:58 PM

Operator LIQUN QIU
Instrument HCTultra

Acquisition Parameters

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Mass Range Mode	Std/Enhanced	Scan Begin	500 m/z	Scan End	1400 m/z
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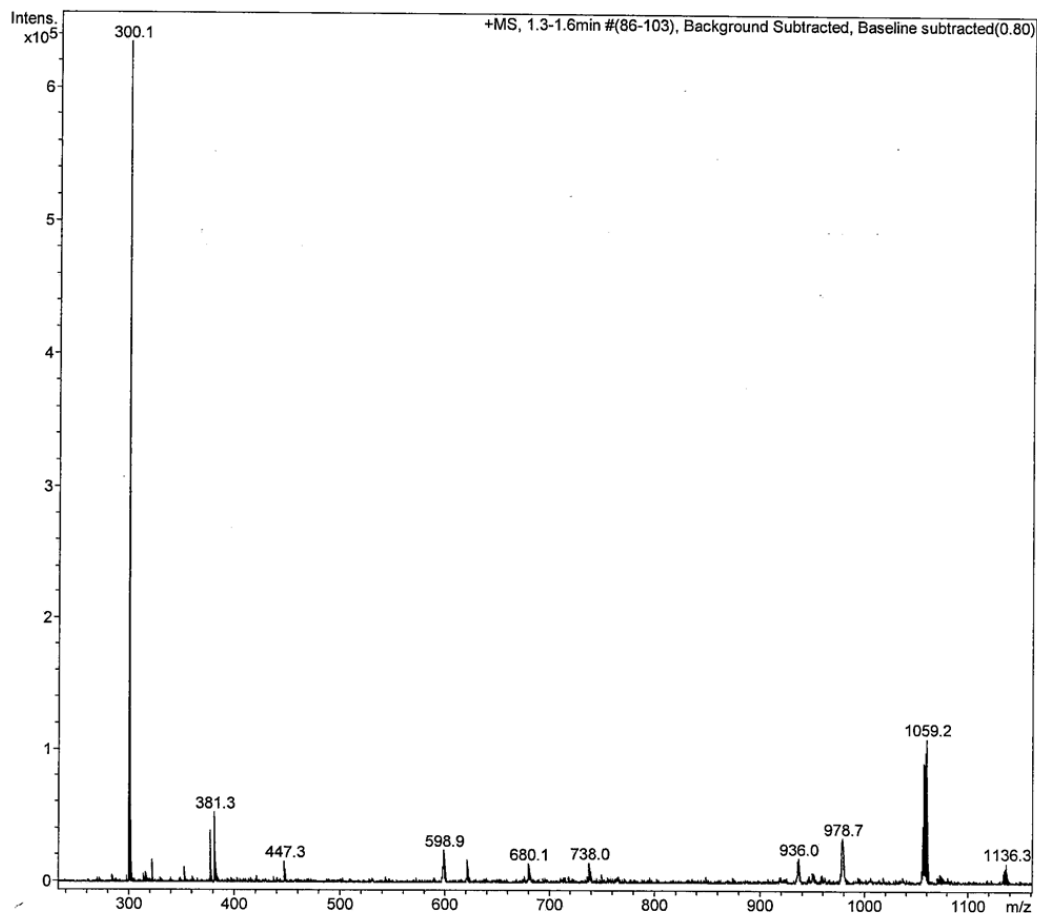


Figure S3. ESI mass spectrum (positive ion mode) of **2**.

Brock MS Facility - Bruker HCT Ultra - LCMS

Analysis Info		Acquisition Date 10/02/2016 7:07:58 PM	
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Method	QL 160105.m	Instrument	HCTultra
Sample Name	160105.m		
Comment			

Acquisition Parameters

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Std/Enhanced	Scan Begin	500 m/z	Scan End	1400 m/z
Capillary Exit	136.0 Volt	Skimmer	40.0 Volt	Trap Drive	209.8
Accumulation Time	43696 μ s	Averages	5 Spectra	Auto MS/MS	off

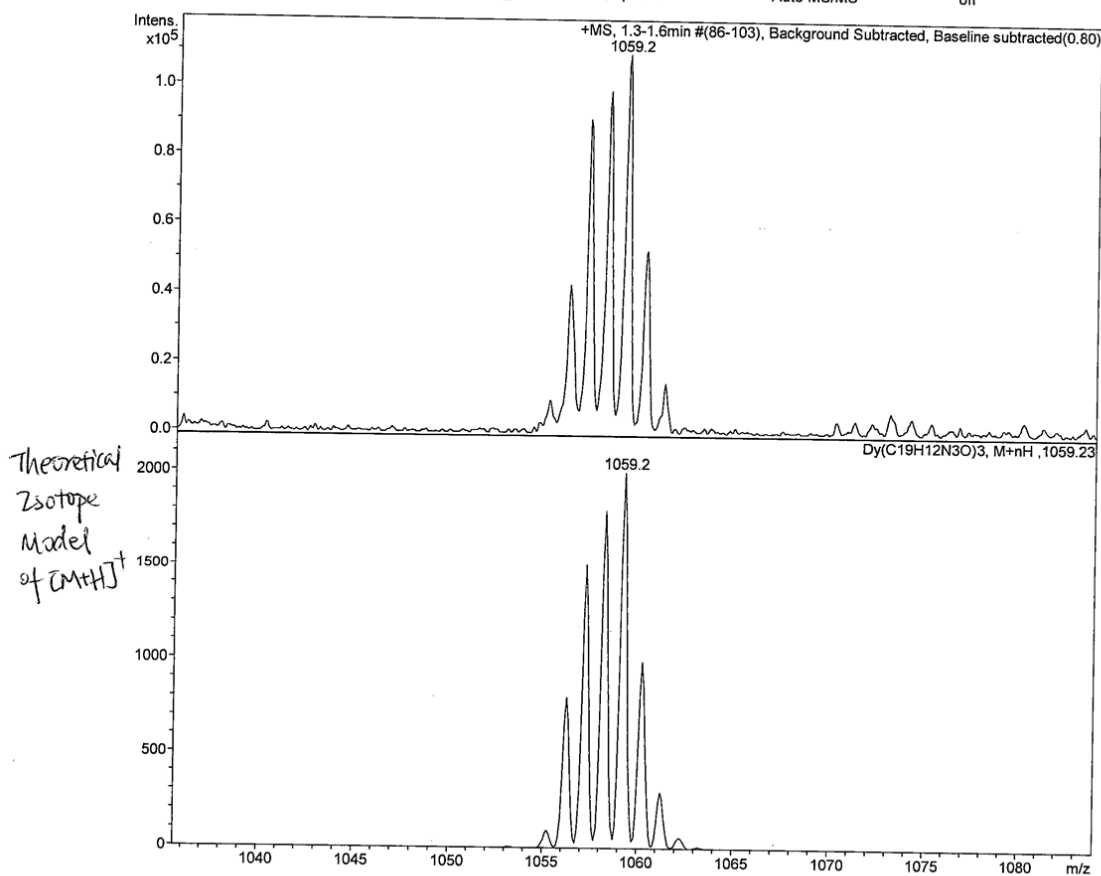


Figure S4. Experimental (top) and theoretical (bottom) isotopic distribution for $[\text{M}+\text{H}]^+$ peak for

Brock MS Facility - Bruker HCT Ultra - LCMS

Analysis Info

Analysis Name D:\Data\16Feb\MLH0136.d
Method QL 160105.m
Sample Name ~~RT 2.47~~
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Acquisition Date 10/02/2016 7:53:20 PM

Operator LIQUN QIU
Instrument HCTultra

Acquisition Parameters

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
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Accumulation Time	2180 μ s	Averages	5 Spectra	Auto MS/MS	off

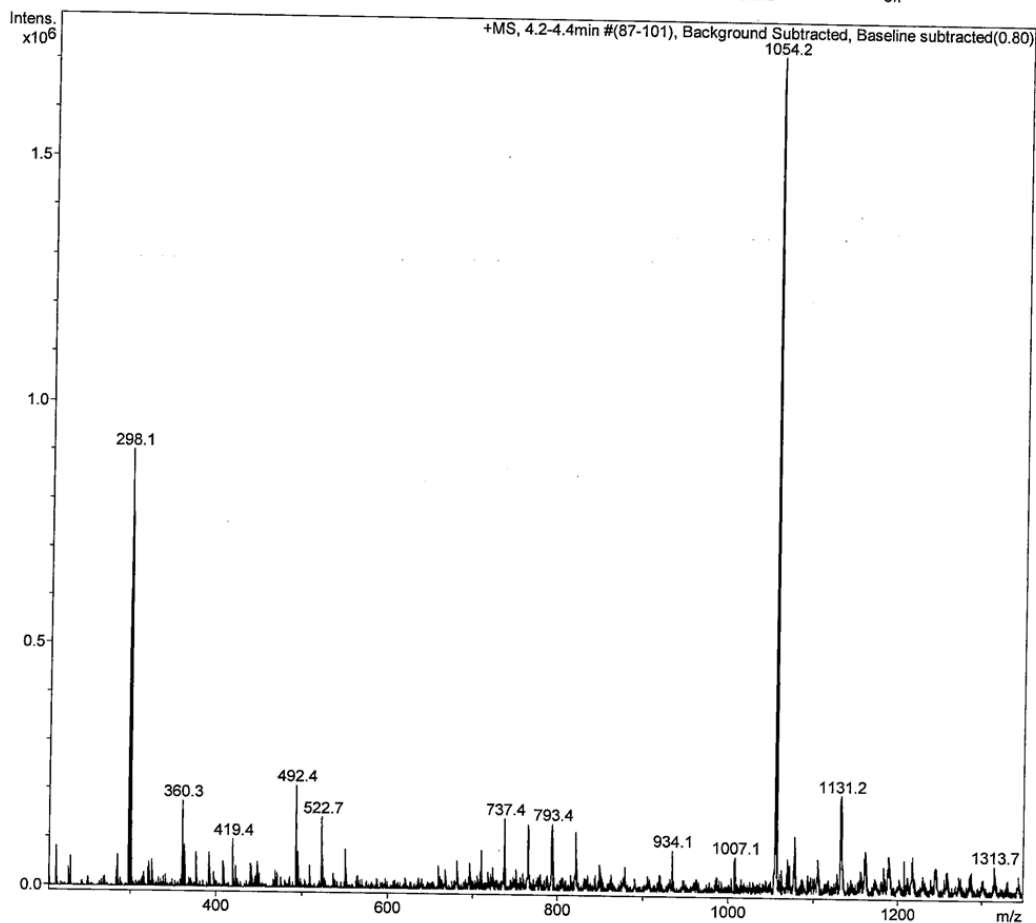


Figure S5. ESI mass spectrum (positive ion mode) of **3**.

Brock MS Facility - Bruker HCT Ultra - LCMS

Analysis Info

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 Sample Name ~~160105.m~~
 Comment

Acquisition Date 10/02/2016 7:53:20 PM

Operator LIQUN QIU
 Instrument HCTultra

Acquisition Parameters

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	Std/Enhanced	Scan Begin	200 m/z	Scan End	1400 m/z
Capillary Exit	106.9 Volt	Skimmer	40.0 Volt	Trap Drive	83.7
Accumulation Time	2180 μ s	Averages	5 Spectra	Auto MS/MS	off

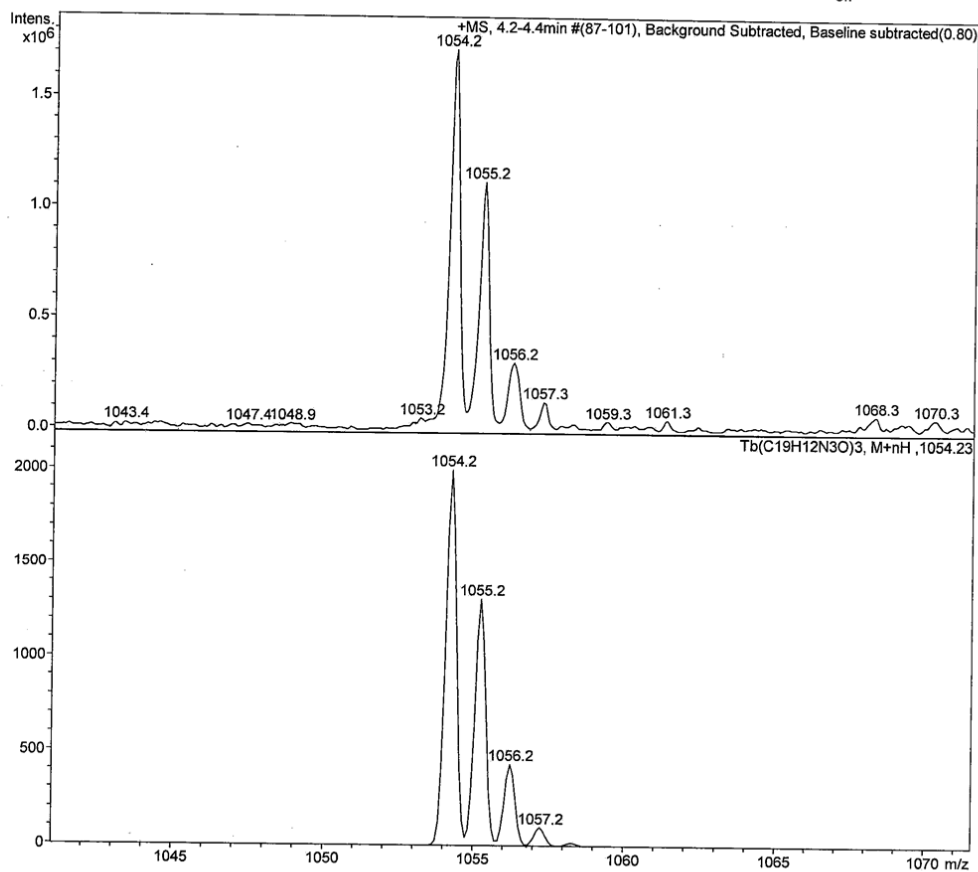


Figure S6. Experimental (top) and theoretical (bottom) isotopic distribution for $[M+H]^+$ peak for

3.

Table S1. Crystal data and structure refinement for **4**.

Empirical formula	C ₆₉ H ₄₂ Ho N ₉ O ₃	
Formula weight	1210.04	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 17.0922(15)$ Å	$\alpha = 90^\circ$.
	$b = 22.4119(17)$ Å	$\beta = 92.427(3)^\circ$.
	$c = 15.7288(14)$ Å	$\gamma = 90^\circ$.
Volume	6019.8(9) Å ³	
Z	4	
Density (calculated)	1.335 Mg/m ³	
Absorption coefficient	1.368 mm ⁻¹	
F(000)	2440	
Crystal size	0.220 x 0.120 x 0.100 mm ³	
Theta range for data collection	1.499 to 27.549°.	
Index ranges	-22 ≤ h ≤ 17, -29 ≤ k ≤ 29, -20 ≤ l ≤ 20	
Reflections collected	55440	
Independent reflections	6963 [R(int) = 0.0859]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6314	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6963 / 306 / 492	
Goodness-of-fit on F ²	1.370	
Final R indices [I > 2σ(I)]	R1 = 0.1087, wR2 = 0.2078	
R indices (all data)	R1 = 0.1398, wR2 = 0.2178	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.828 and -1.366 e.Å ⁻³	

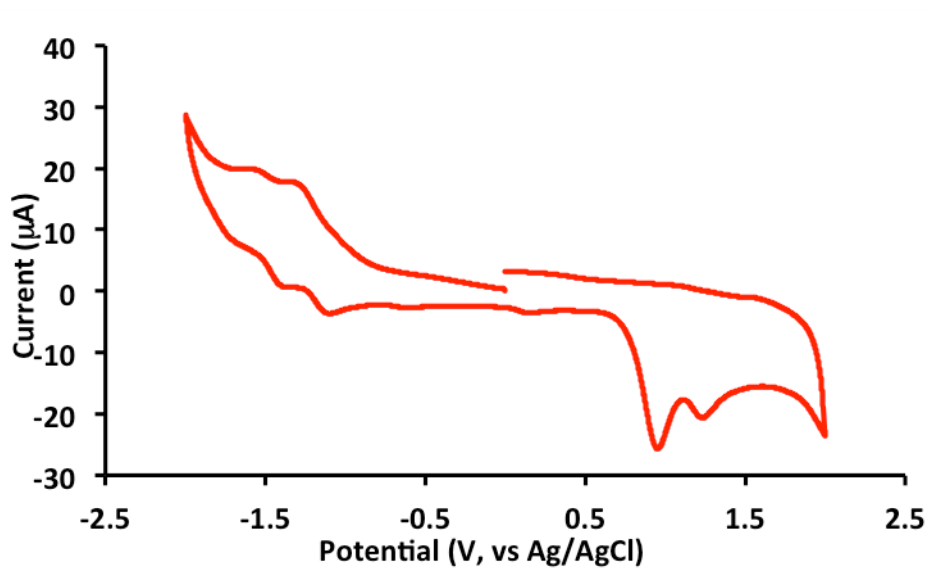


Figure S7. Cyclic voltammogram of **2** in CH_2Cl_2 .

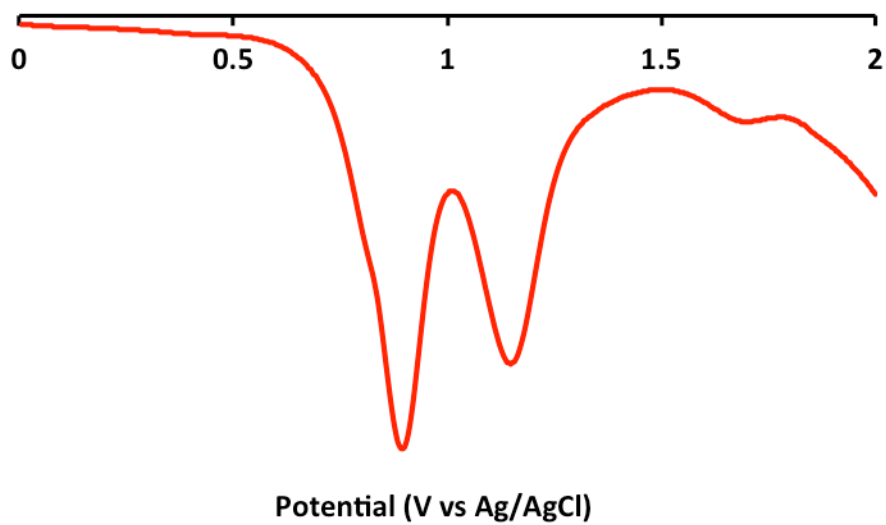


Figure S8. DPV (anodic) of **2** in CH_2Cl_2 .

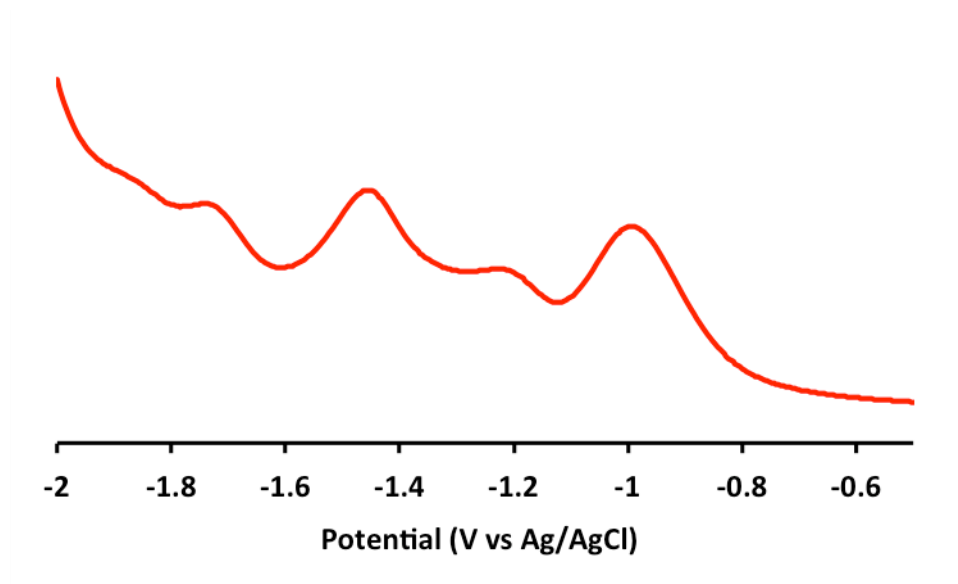


Figure S9. DPV (cathodic) of **2** in CH_2Cl_2 .

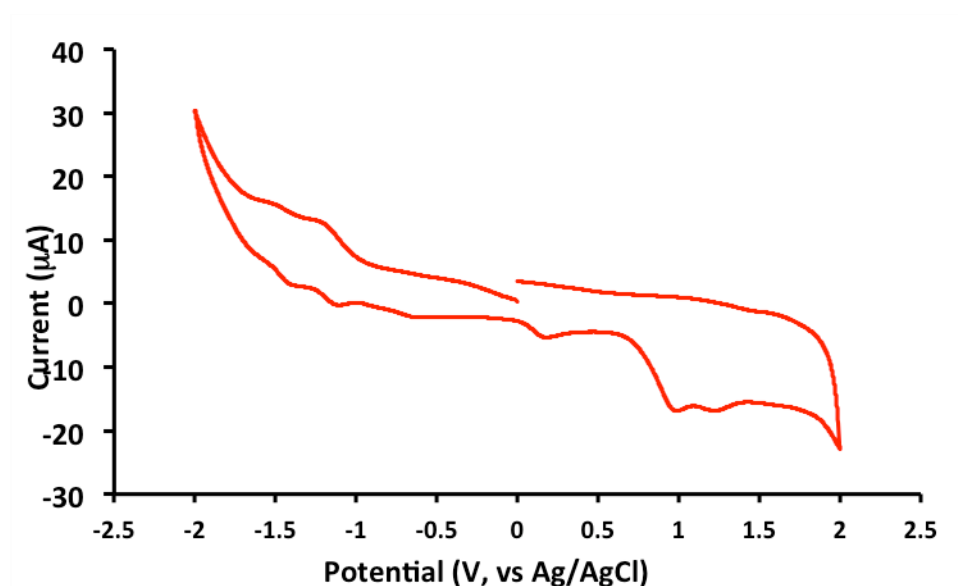


Figure S10. Cyclic voltammogram of **3** in CH_2Cl_2 .

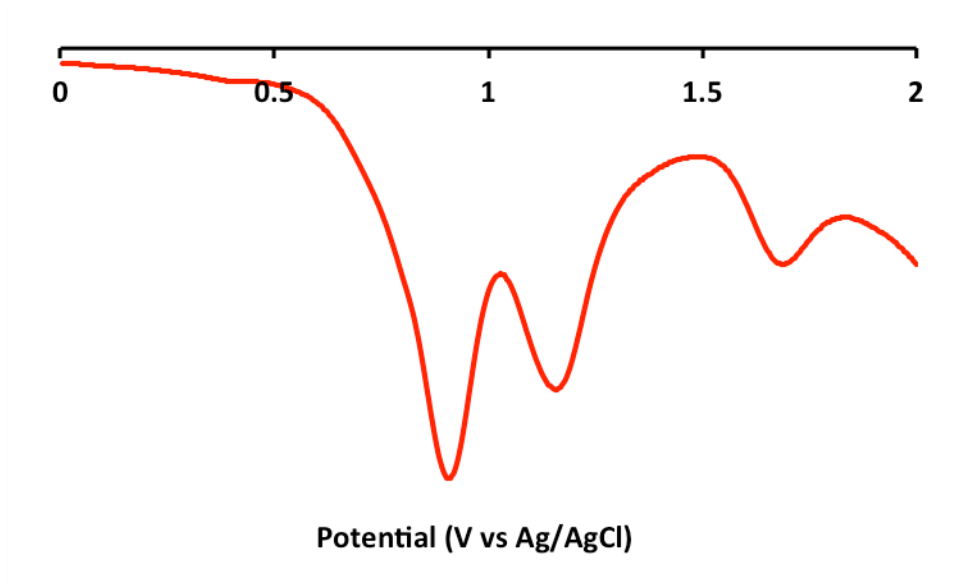


Figure S11. DPV (anodic) of **3** in CH_2Cl_2 .

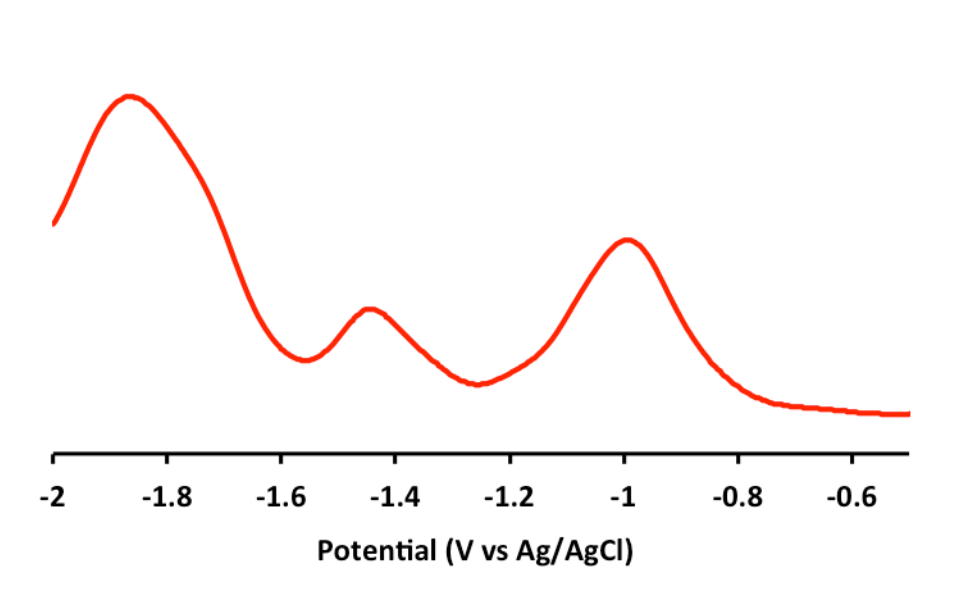


Figure S12. DPV (cathodic) of **3** in CH_2Cl_2 .

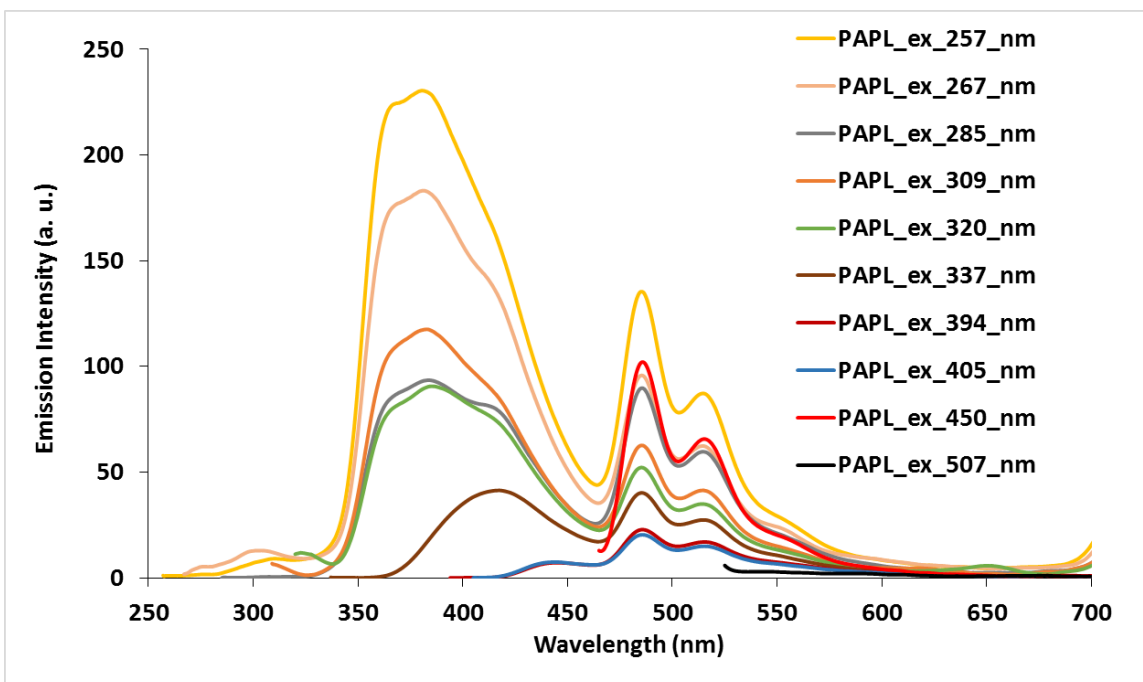


Figure S13. Emission profile of **papl** at different λ_{exc} (257 to 507 nm) in DCM at room temperature.

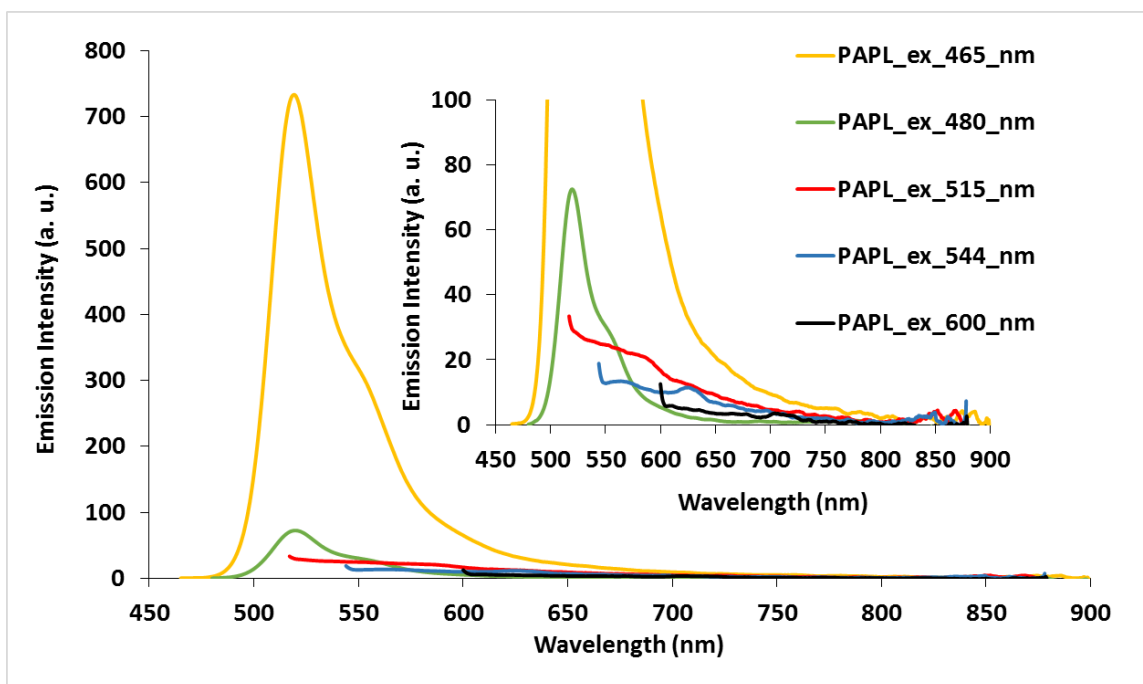


Figure S14. Emission profile of **papl** at different λ_{exc} (465 to 600 nm) in DCM at room temperature.

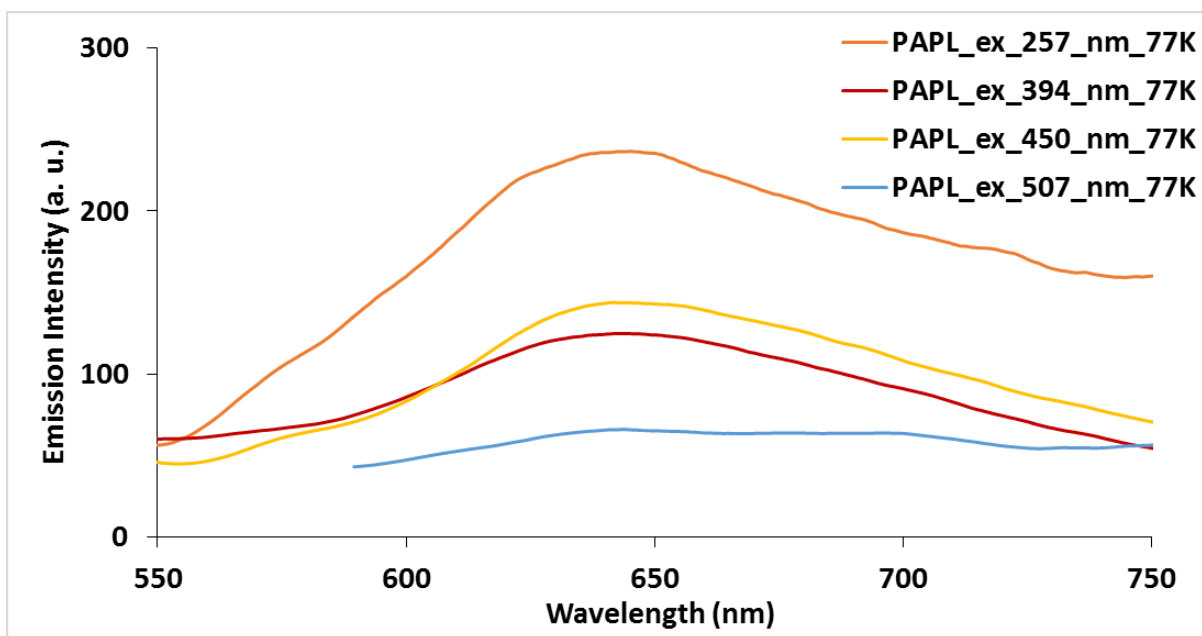


Figure S15. Emission profile of **papl** at different λ_{exc} (257 to 507 nm) in DCM at 77 K; $\lambda_{\text{max em}} = 645$ nm.

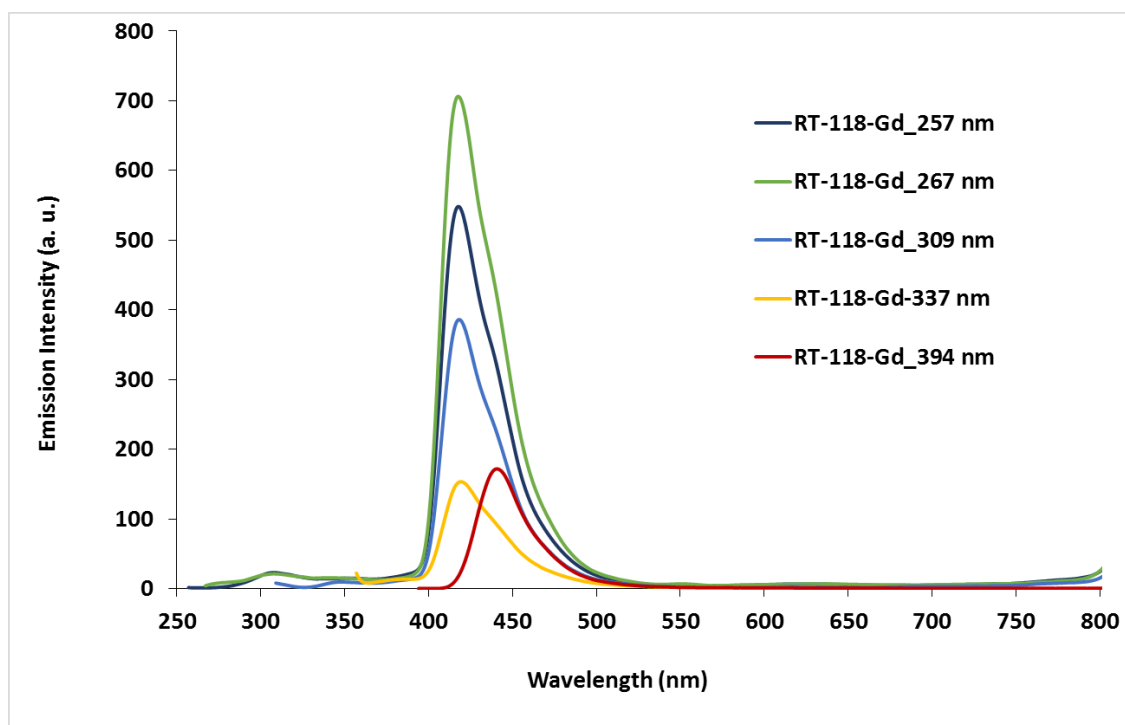


Figure S16. Emission profile of **1** at different λ_{exc} in DCM at room temperature; $\lambda_{\text{max em}} = 419$ nm. No emission was observed when $\lambda_{\text{exc}} = 517$, $\lambda_{\text{exc}} = 544$, and $\lambda_{\text{exc}} = 600$.

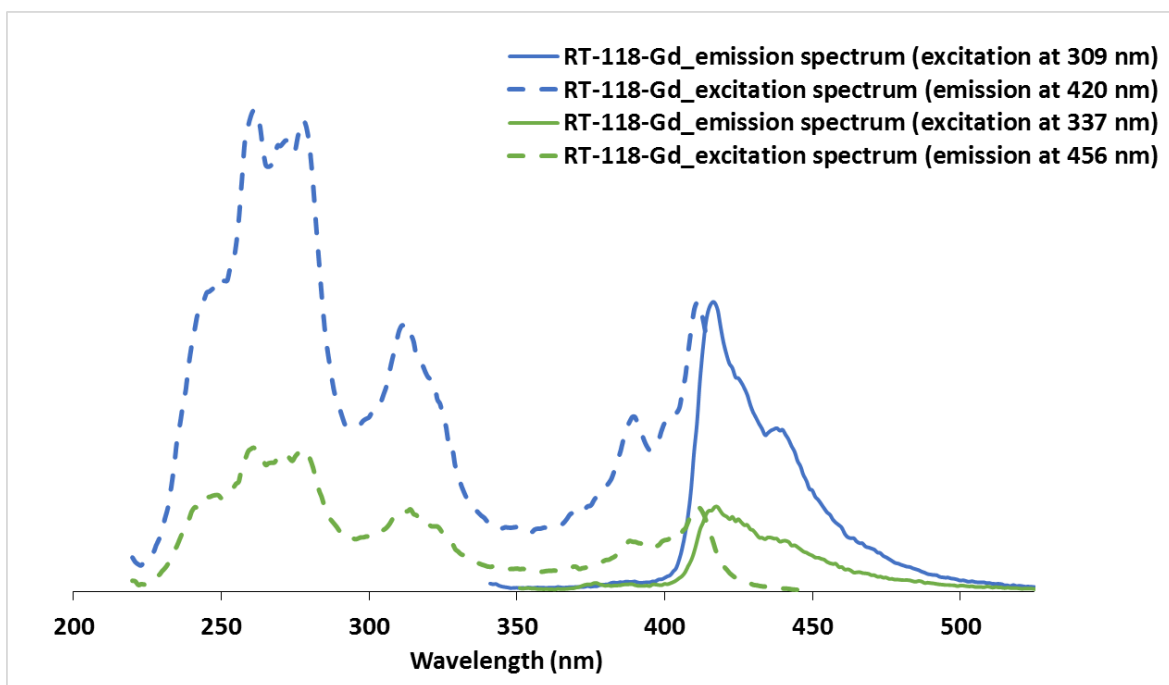


Figure S17. Emission and excitation profiles of **1** in DCM at room temperature.

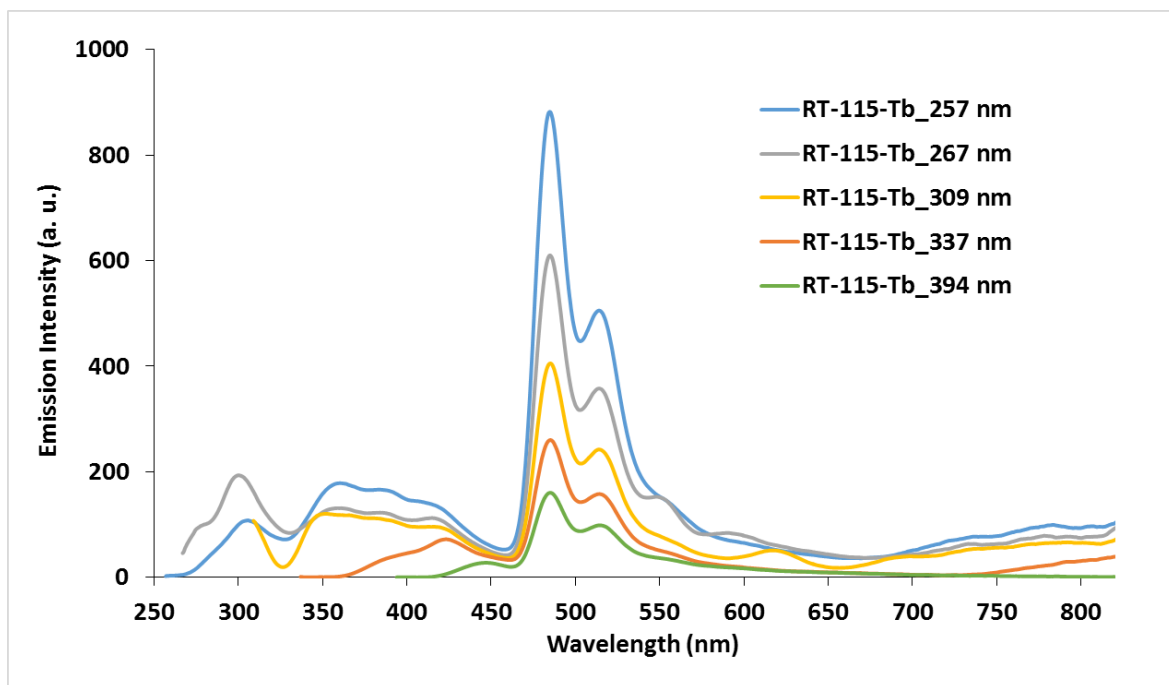


Figure S18. Emission profile of **3** at different λ_{exc} in DCM at room temperature; $\lambda_{\text{max em}}$ (nm): 419, 485, 515. No emission was observed when $\lambda_{\text{exc}} = 517$, $\lambda_{\text{exc}} = 544$, and $\lambda_{\text{exc}} = 600$.

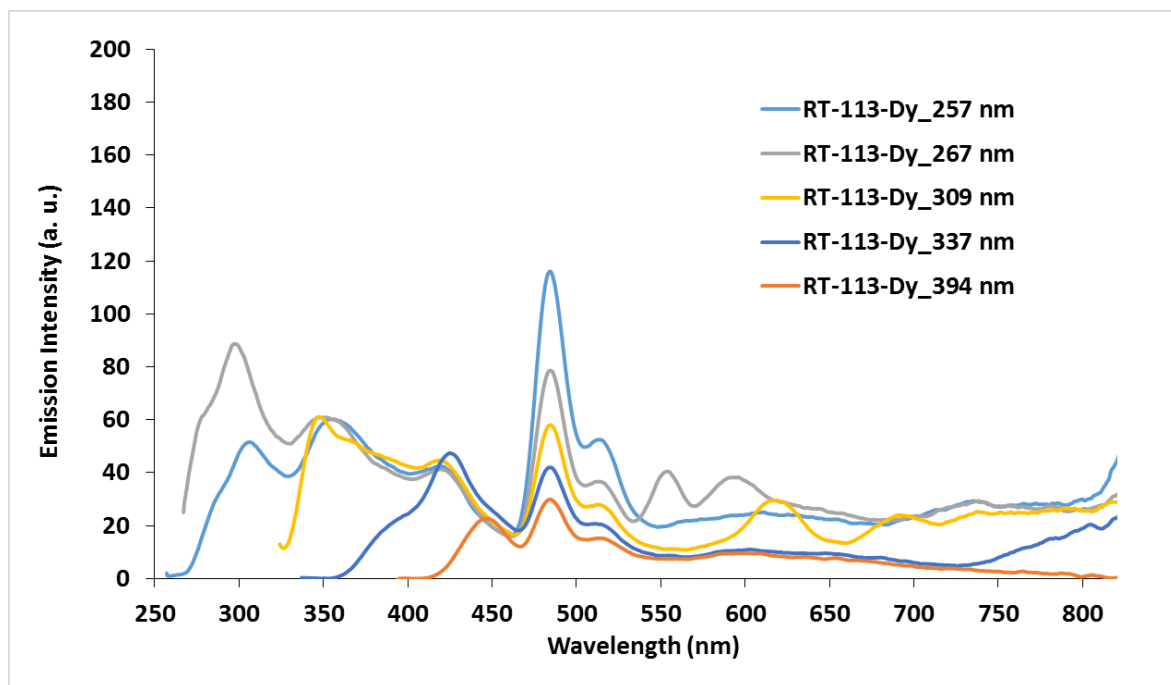


Figure S19. Emission profile of **2** at different λ_{exc} in DCM at room temperature; $\lambda_{\text{max em}}$ (nm): 419, 485, 515. Because of the very weak emission of the compound, emission of the solvent is observed – see the comparative figures below (Figures S21-S24). No emission was observed when $\lambda_{\text{exc}} = 517$, $\lambda_{\text{exc}} = 544$, and $\lambda_{\text{exc}} = 600$.

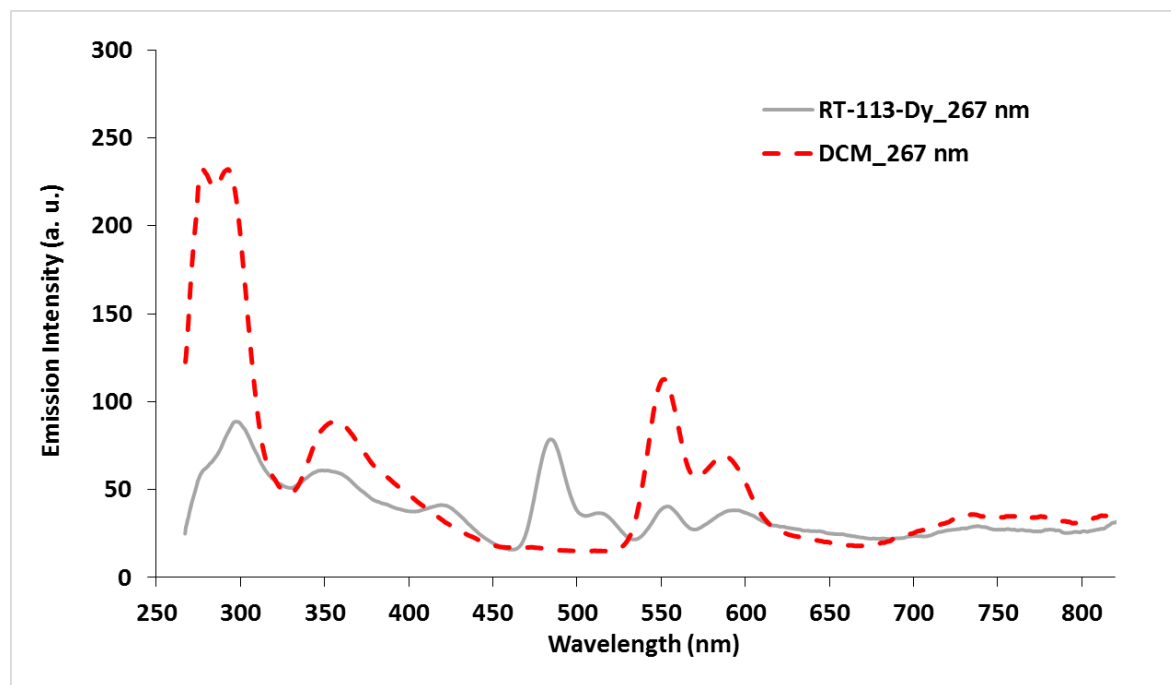


Figure S20. Emission profiles of **2** in DCM (grey line) and the solvent DCM (dashed red line) at room temperature; $\lambda_{\text{exc}} = 267$ nm.

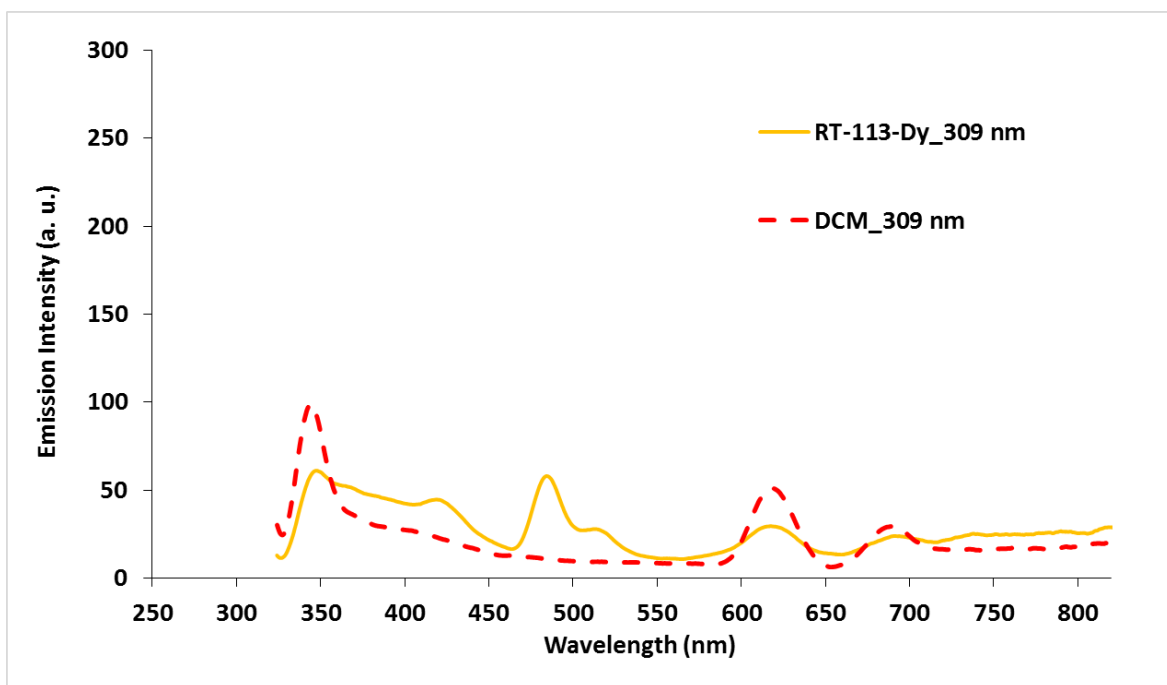


Figure S21. Emission profiles of **2** in DCM (yellow line) and the solvent DCM (red dashed line) at room temperature; $\lambda_{\text{exc}} = 309$ nm.

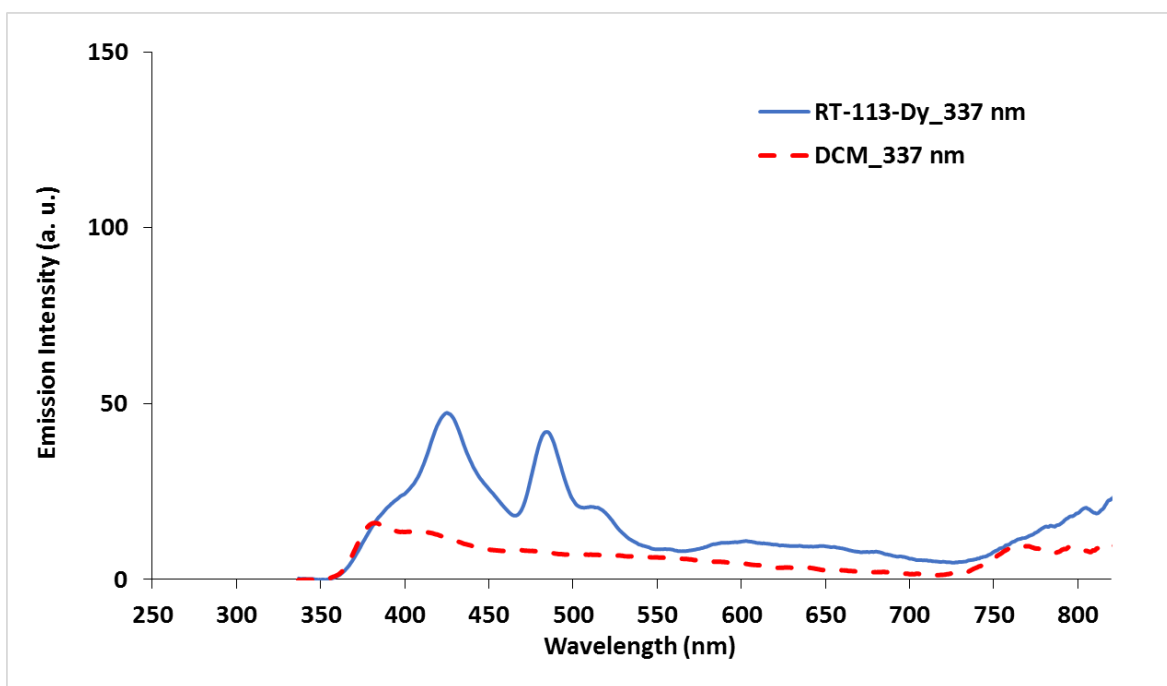


Figure S22. Emission profiles of **2** in DCM (blue line) and the solvent DCM (red dashed line) at room temperature; $\lambda_{\text{exc}} = 337$ nm.

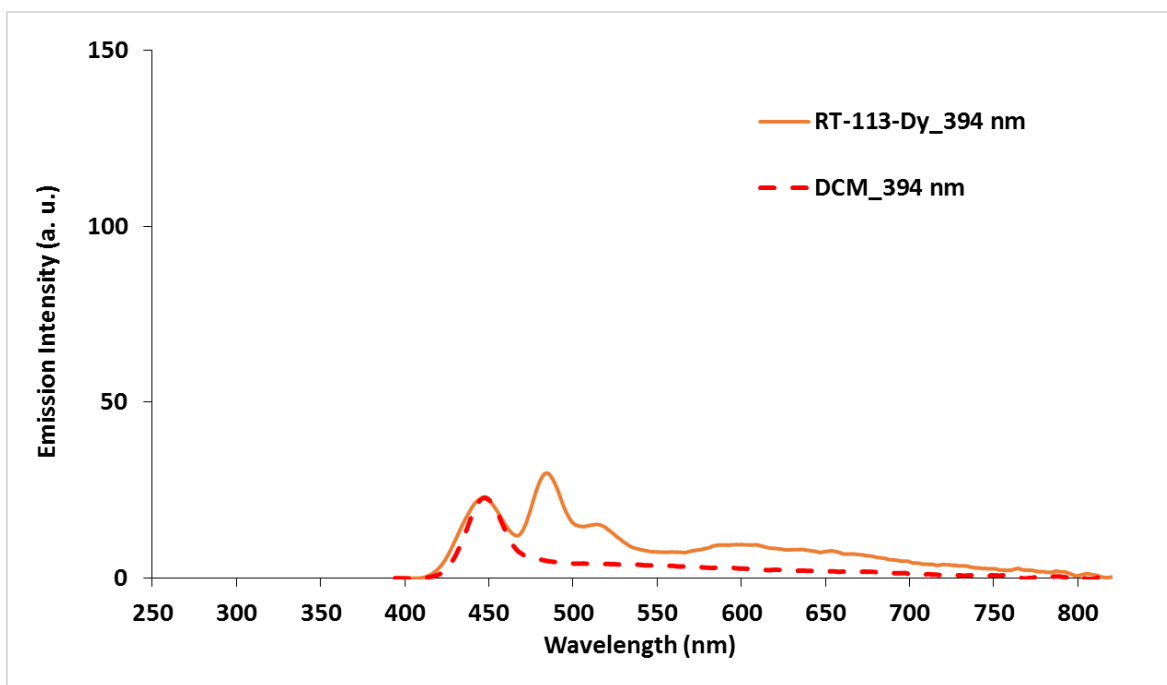


Figure S23. Emission profiles of **2** in DCM (orange line) and the solvent DCM (red dashed line) at room temperature; $\lambda_{\text{exc}} = 394$ nm.

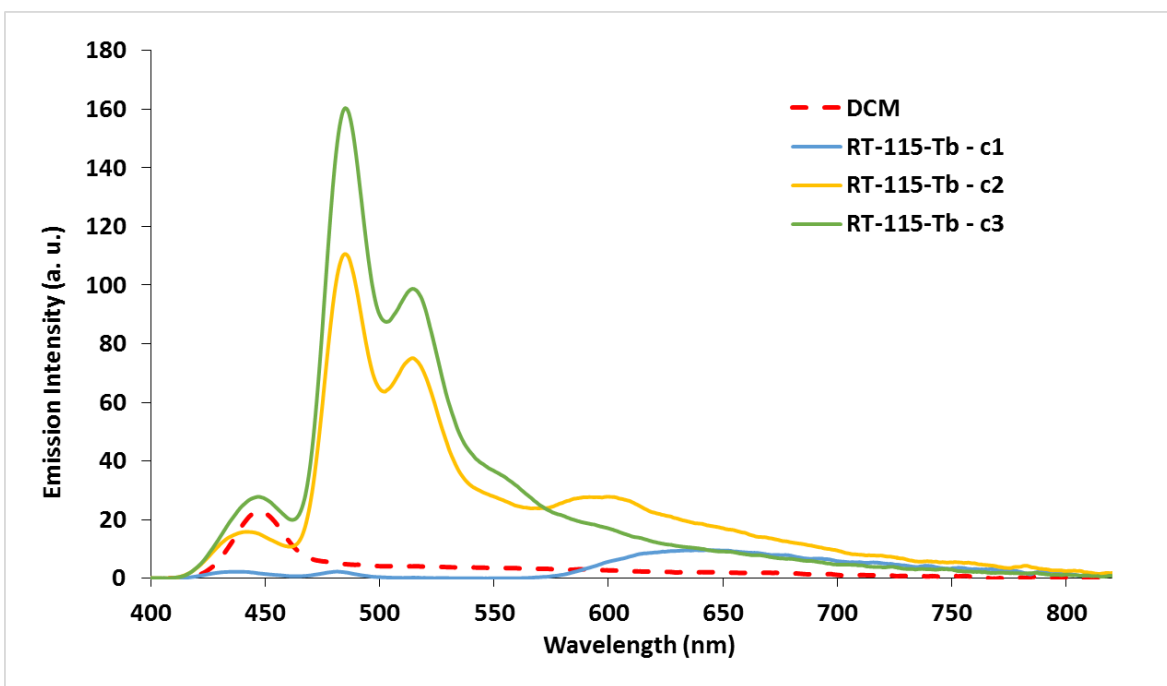


Figure S24. Emission profile of **3** at different concentrations in DCM at room temperature; $\lambda_{\text{exc}} = 394$ nm; c1 = 1.0×10^{-4} M; c2 = 5.7×10^{-5} M; c3 = 9.5×10^{-6} M.

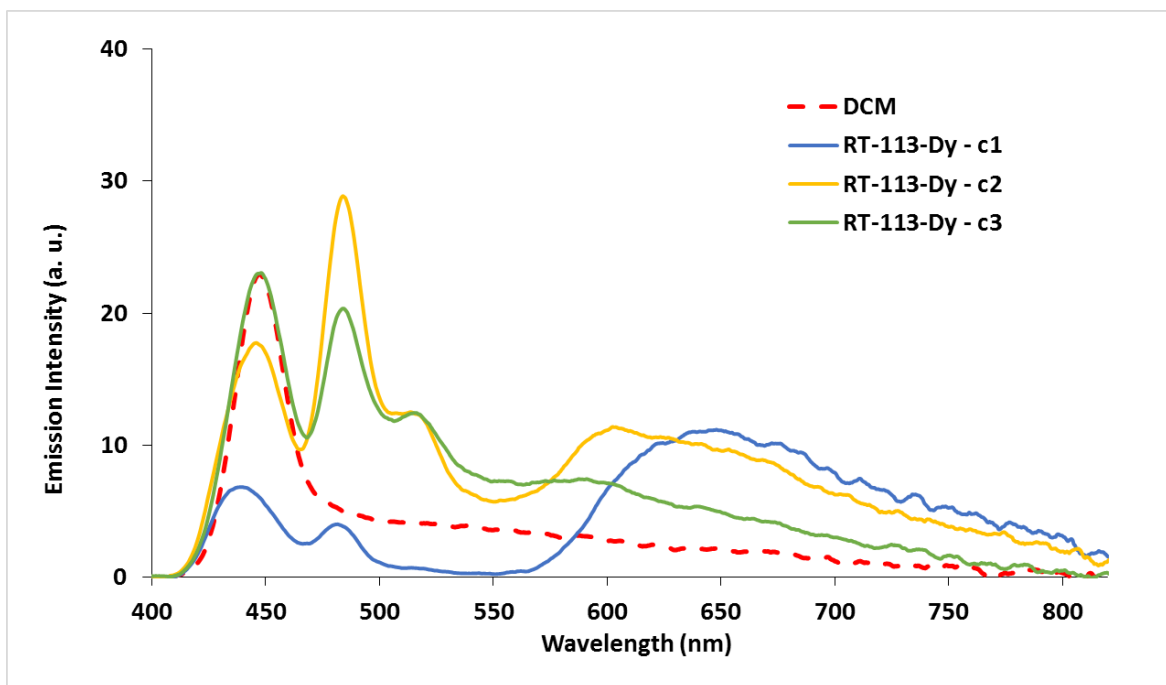


Figure S25. Emission profile of **2** at different concentrations in DCM at room temperature; $\lambda_{\text{exc}} = 394 \text{ nm}$; $c1 = 2.1 \times 10^{-4} \text{ M}$; $c2 = 4.2 \times 10^{-5} \text{ M}$; $c3 = 6.9 \times 10^{-6} \text{ M}$

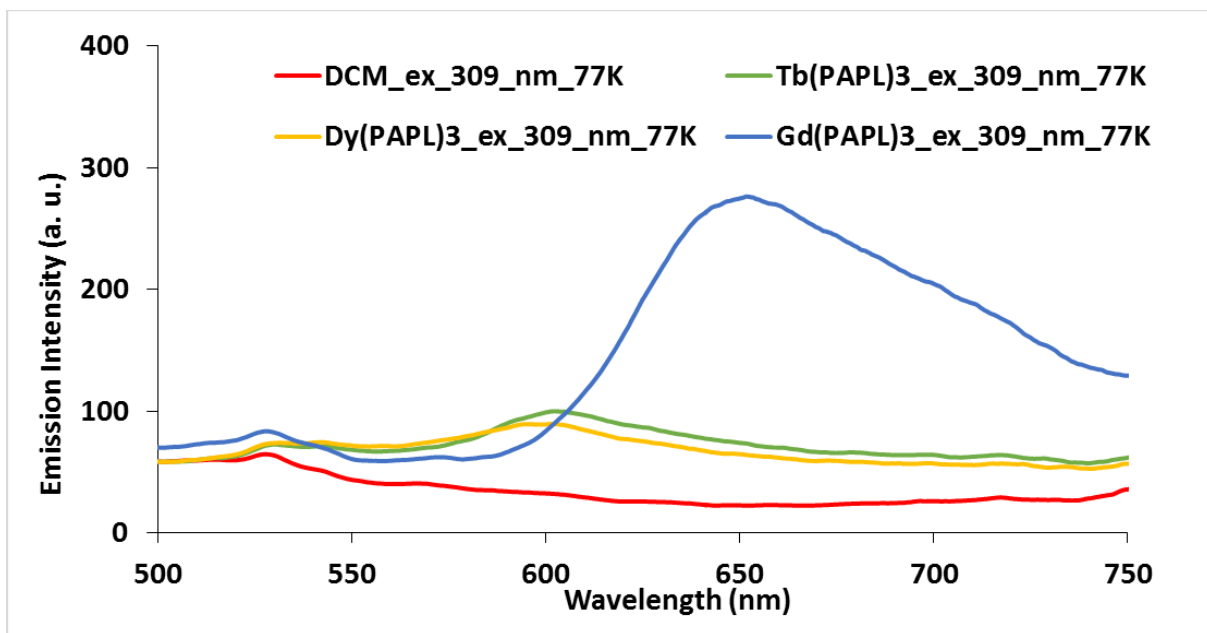


Figure S26. Emission profile of **1** (blue line), **2** (yellow line), **3** (green line) in DCM and DCM (red line) at 77 K; $\lambda_{\text{exc}} = 309 \text{ nm}$.