Highly Luminescent Sm(III) Complexes with Intra-Ligand Charge-Transfer Sensitization and the Effect of Solvent Polarity on their Luminescent Properties

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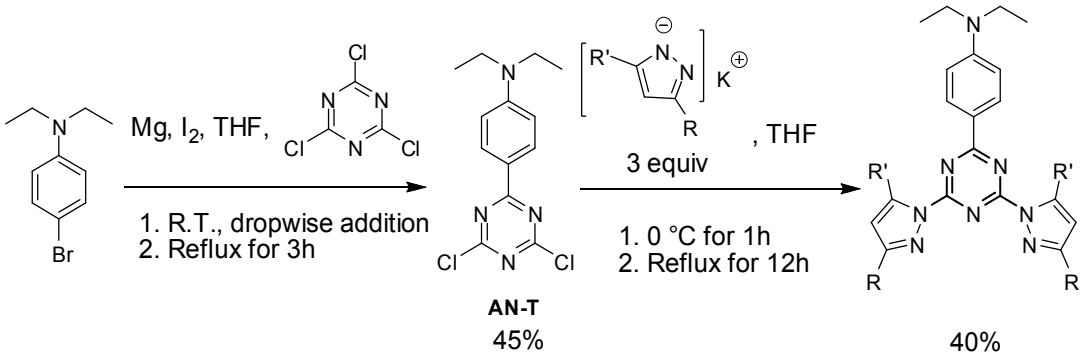
Supporting Information

Contents

Experimental Section

Materials and Methods. 2-thenoyltrifluoroacetonate (tta) lanthanide salt Eu(tta)3·H2O was purchased from Alfa Aesar and Sm(tta)3·H2O was synthesized according to literature procedures with anhydrous $SmCl_3$ (99.99%) and 2-thenoyltrifluoroacetone (99%) from Aldrich. THF was dried with sodium metal and benzophenone. CHROMASOLV® solvents, sulfuric acid concentrate (0.1 M) and quinine sulfate from Sigma-Aldrich were used for photophysical measurements. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc.

Absorption spectra of ligands and complexes were measured with an HP UV-8453 spectrophotometer. Steady-state room temperature photoluminescence measurements were performed with an Edinburgh Instrument FLSP920 spectrophotometer equipped with a Xe900 continuous xenon lamp, μF920 microsecond flashlamp and a single photon counting photomultiplier tube. Spectra were corrected with the bundled F900 software. Solution-state measurements were conducted using quartz cuvettes of 10 mm path length. Low temperature (77 K) solid- and solution-state measurements were measured using a nitrogen cryostat OptistatDN-V2 from Oxford Instruments. The relative quantum yields were referenced with quinine sulfate in 0.1 M sulfuric acid (Φ = 0.577) and absolute quantum yields were measured using a demountable integrating sphere from Edinburgh Photonics and the value was calculated using its F900 software.



*Scheme S1 Syntheses of ligands **1-3**.*

Syntheses of **1**, **2**, **3**. *N*,*N*-diethylaniline was slowly added into a THF solution of magnesium turnings with catalytic amount of iodine. The solution was refluxed for 3 hours before cooling to room temperature. The Grignard reagent was then dropped into a THF solution of cyanuric chloride at 4 °C and stirred at 4 °C for 4 more hours. The reaction mixture was quenched with saturated ammonium chloride and extracted with diethyl ether and water. The organic portion was evaporated and **AN-T** was obtained by column chromatography using hexane and dichloromethane (v:v/3:1). 3.5 equivalents of 3,5-dimethylpyrazole were deprotonated by refluxing with potassium metal in THF for 3 hours and cooled. **AN-T** in THF was added at room temperature and stirred for a further hour before refluxing overnight. The solvent mixture was subjected to extraction with DCM and water. The organic portion was evaporated and **1** was obtained by column chromatography using ethyl acetate as the eluent. **2** and **3** were synthesized similarly using 3-methylpyrazole and pyrazole respectively.

Syntheses of complexes. Ln(tta)3·3H2O and the ligand was mixed in a 1:1 ratio in a solution of methanol and stirred at 50 °C overnight. The solvent was subsequently evaporated and the residue was redissolved in minimal amount of diethyl ether. The product was obtained as a yellow solid by repeated precipitation with n-hexanes. Yield: Average ~80%. ESI-MS: *m/z*: 1010 [**Sm-1**-tta]$^+$; *m/z*: 982 [**Sm-2**-tta]$^+$; *m/z*: 954 [**Sm-3**-tta]$^+$.

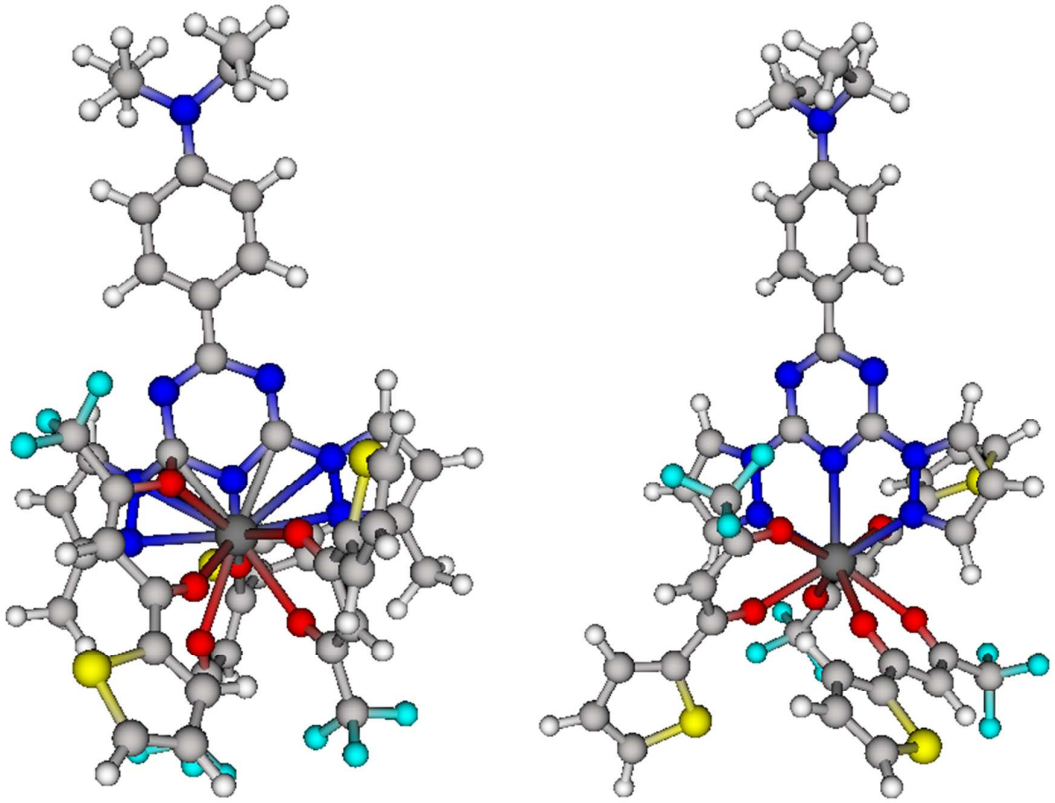


Figure S1 Optimized structures of **Sm**-**2** (left) and **Sm**-**3** (right).

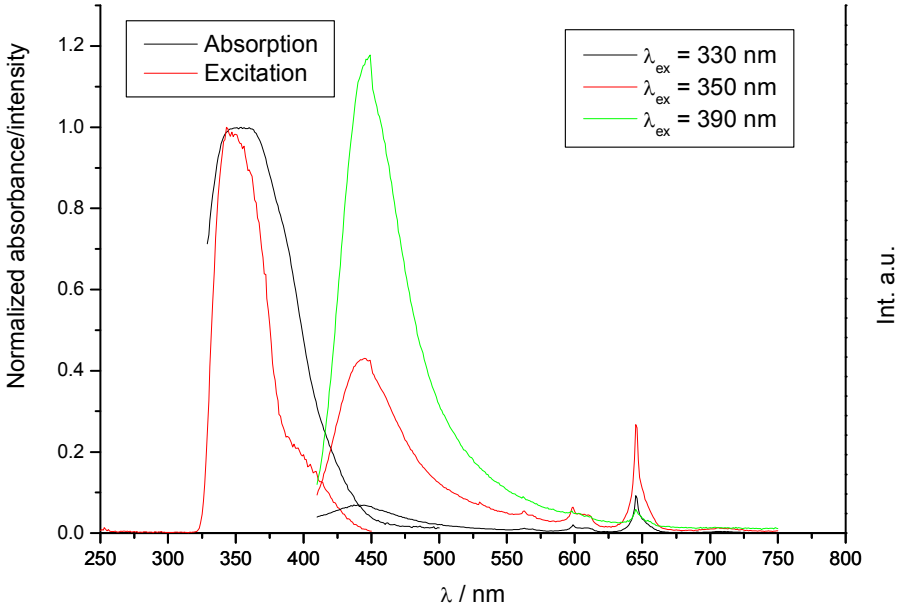


Figure S2 **Sm**-**1** in acetone.

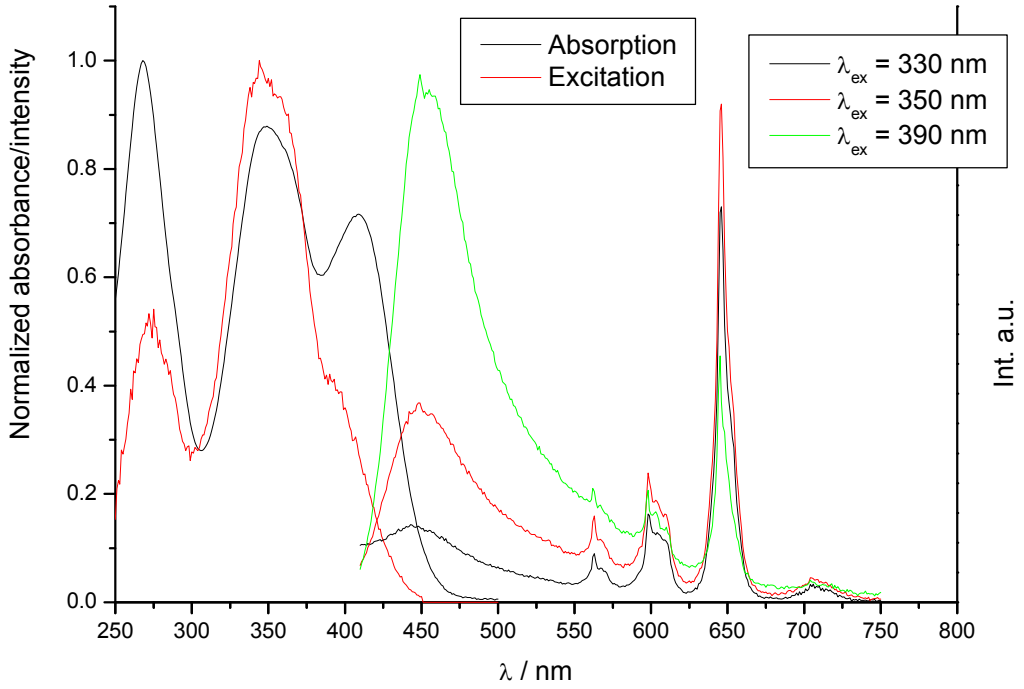


Figure S3 **Sm-1** in acetonitrile.

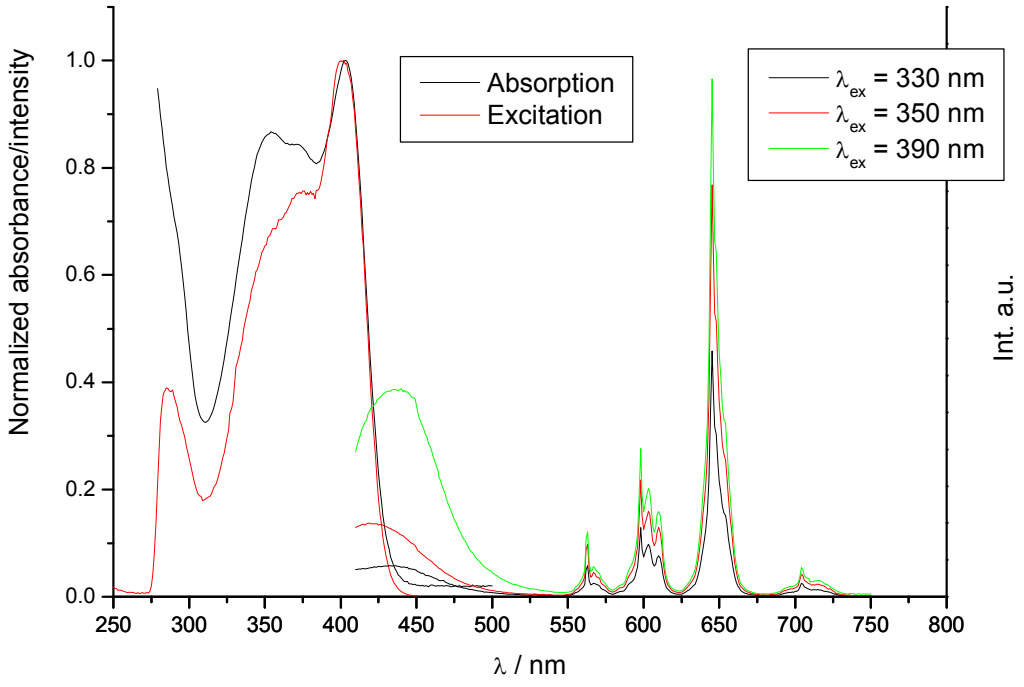


Figure S4 **Sm-1** in benzene.

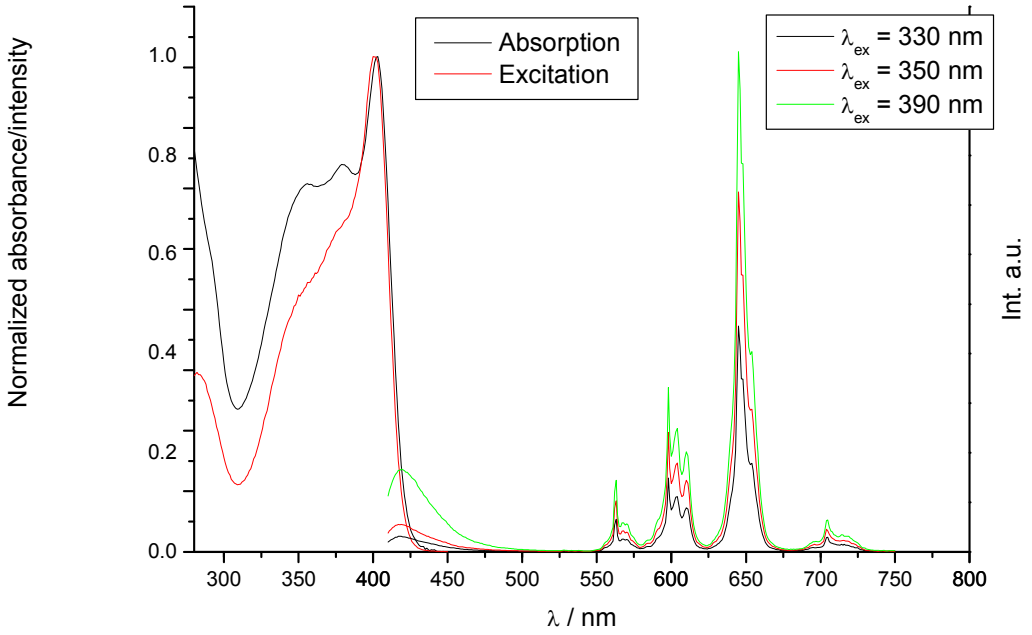


Figure S5 **Sm-1** in carbon tetrachloride.

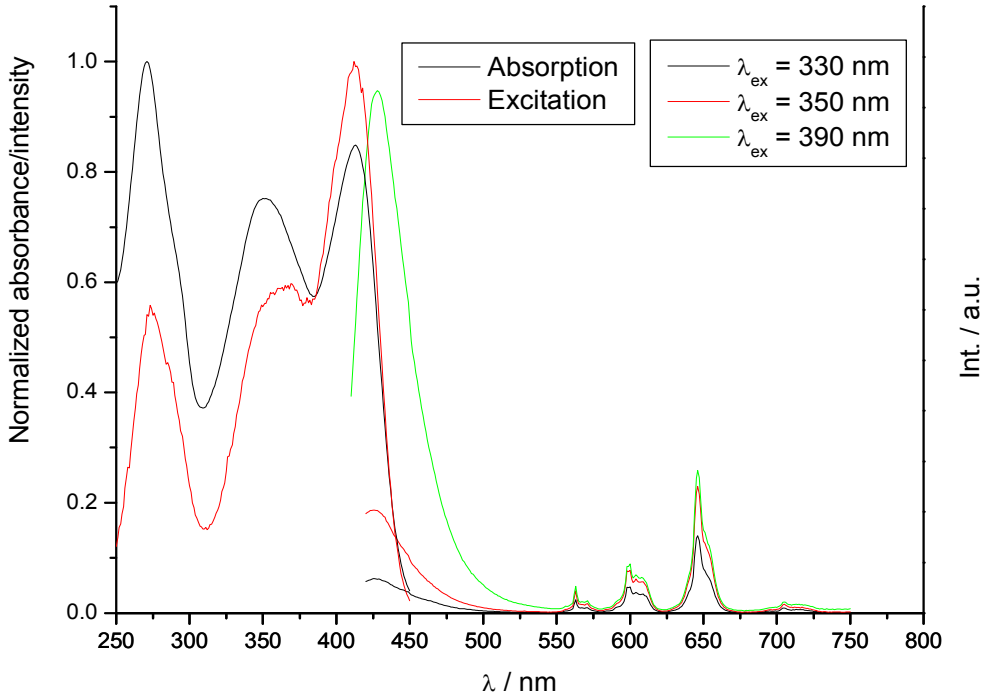


Figure S6 **Sm-1** in chloroform.

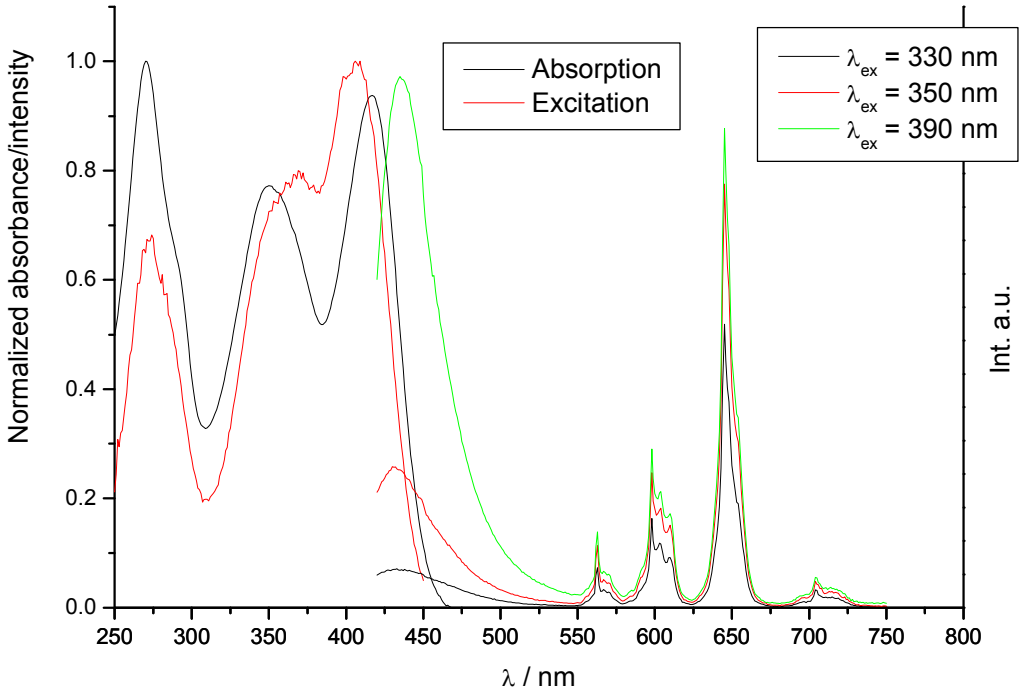


Figure S7 **Sm-1** in dichloromethane.

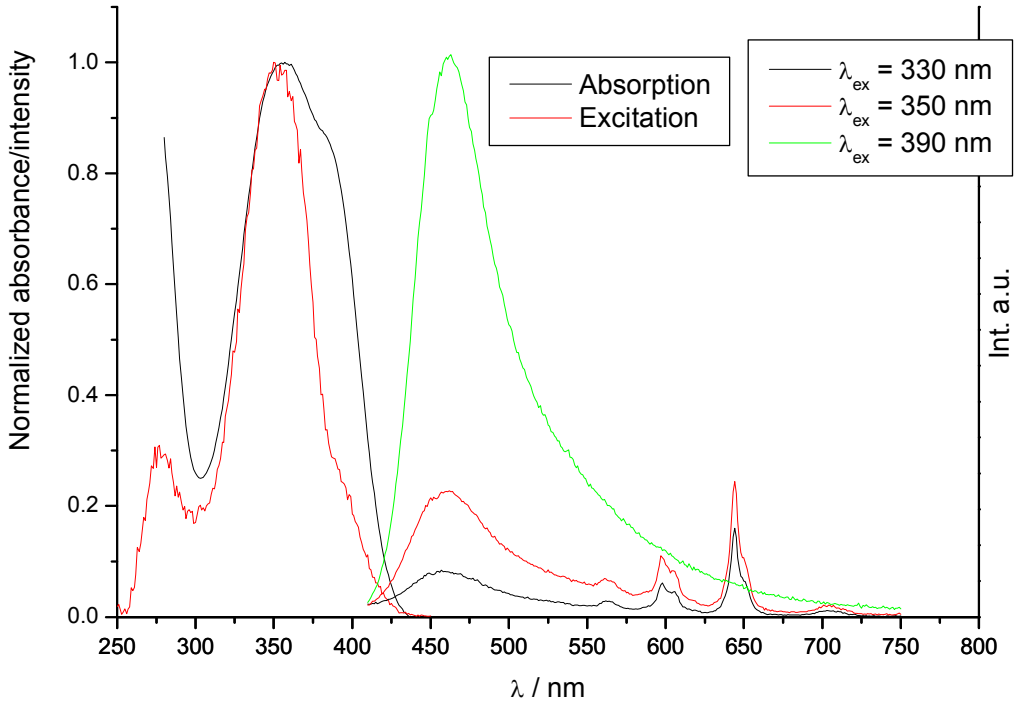


Figure S8 **Sm-1** in dimethyl sulfoxide.

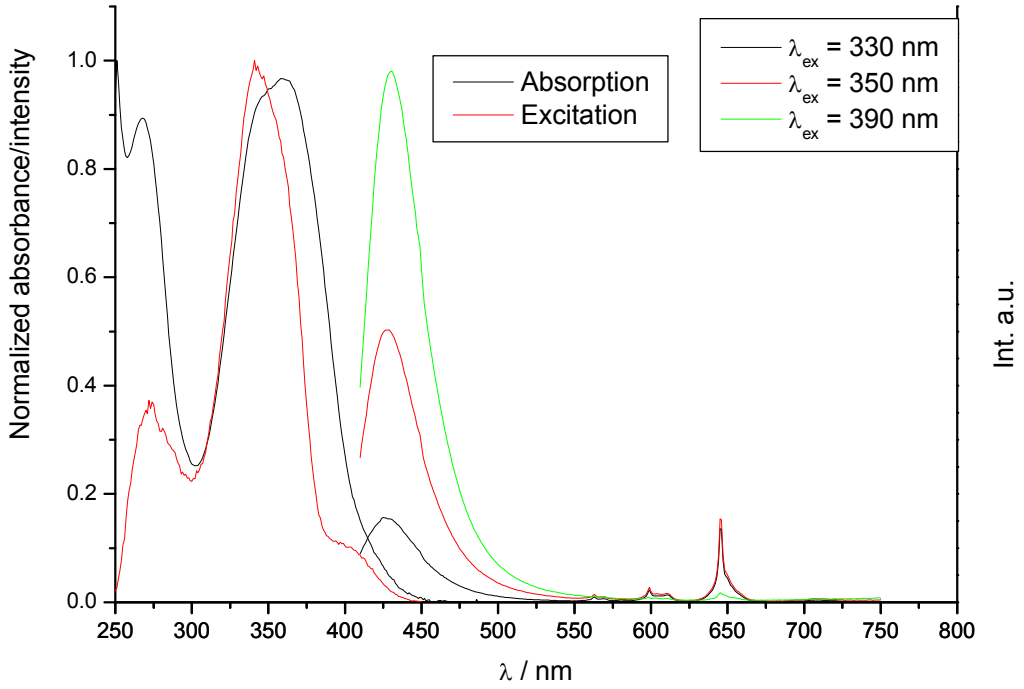


Figure S9 **Sm-1** in ethyl acetate.

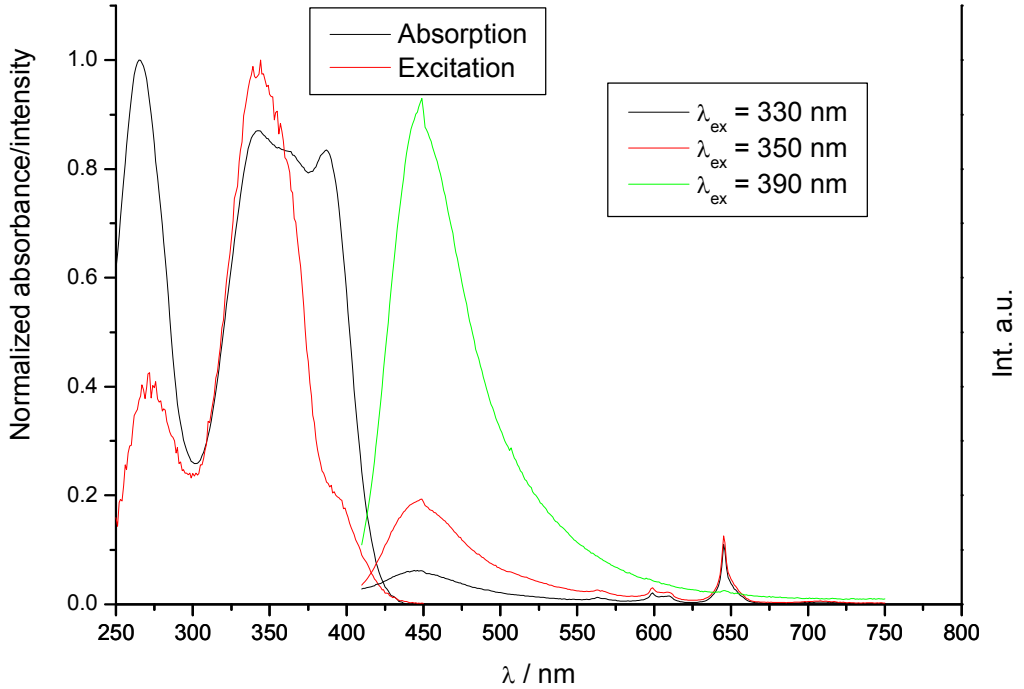


Figure S10 **Sm-1** in isopropanol.

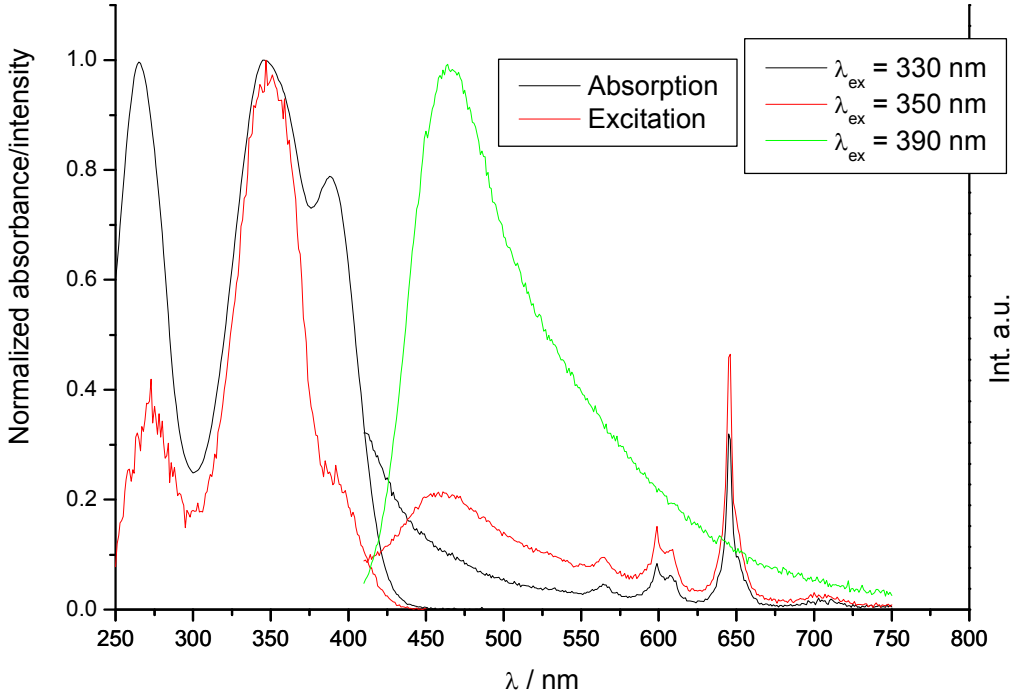


Figure S11 **Sm-1** in methanol.

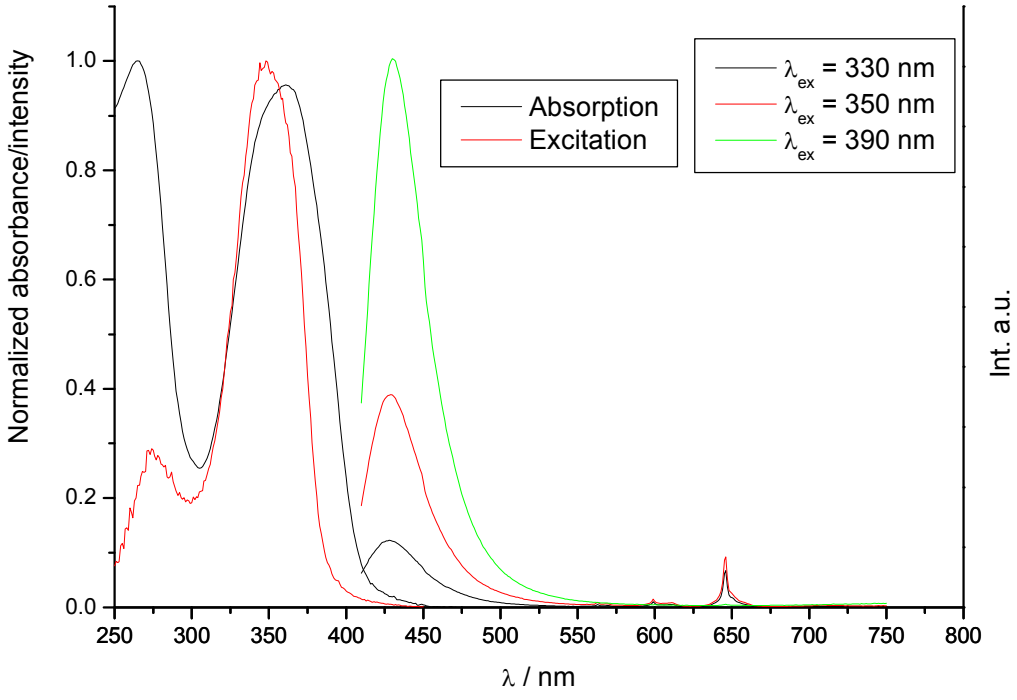


Figure S12 **Sm-1** in tetrahydrofuran.

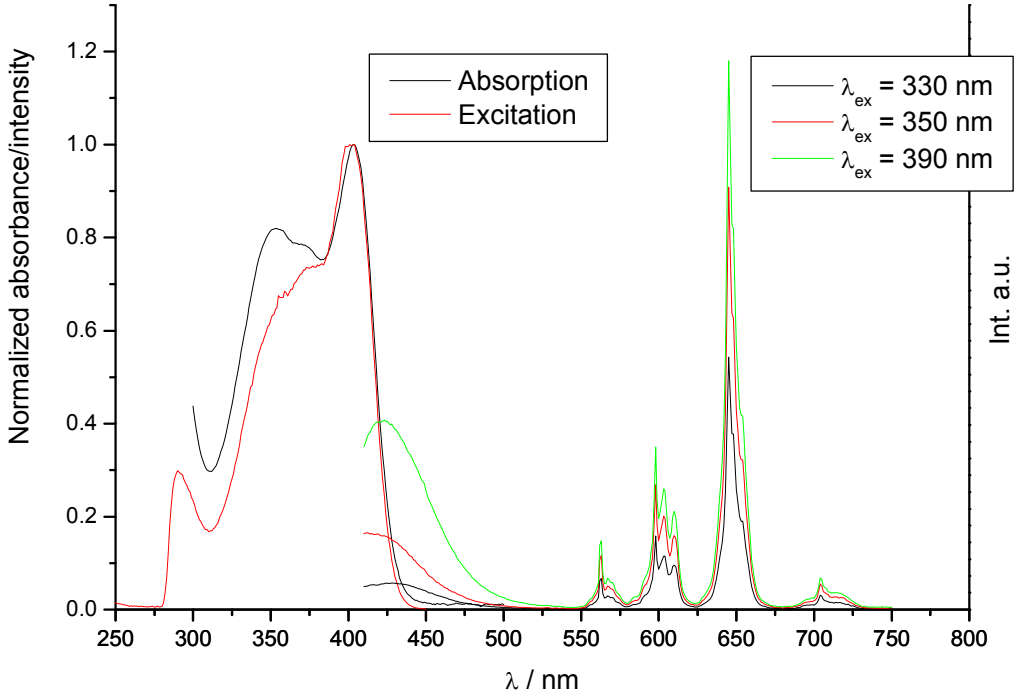


Figure S13 **Sm-1** in toluene.

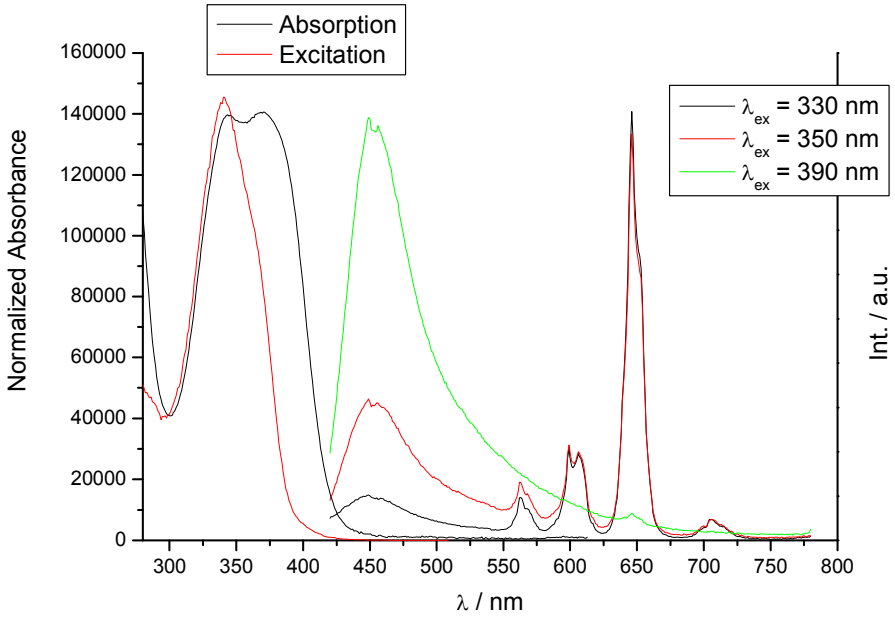


Figure S14 **Sm-2** in acetone.

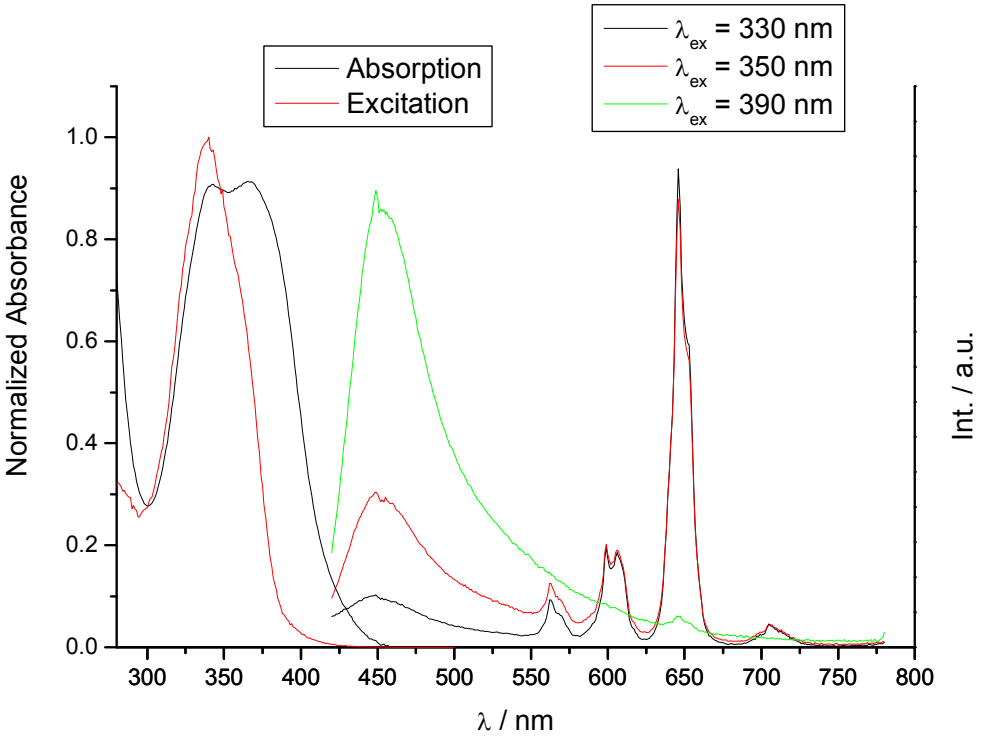


Figure S15 **Sm-2** in acetonitrile.

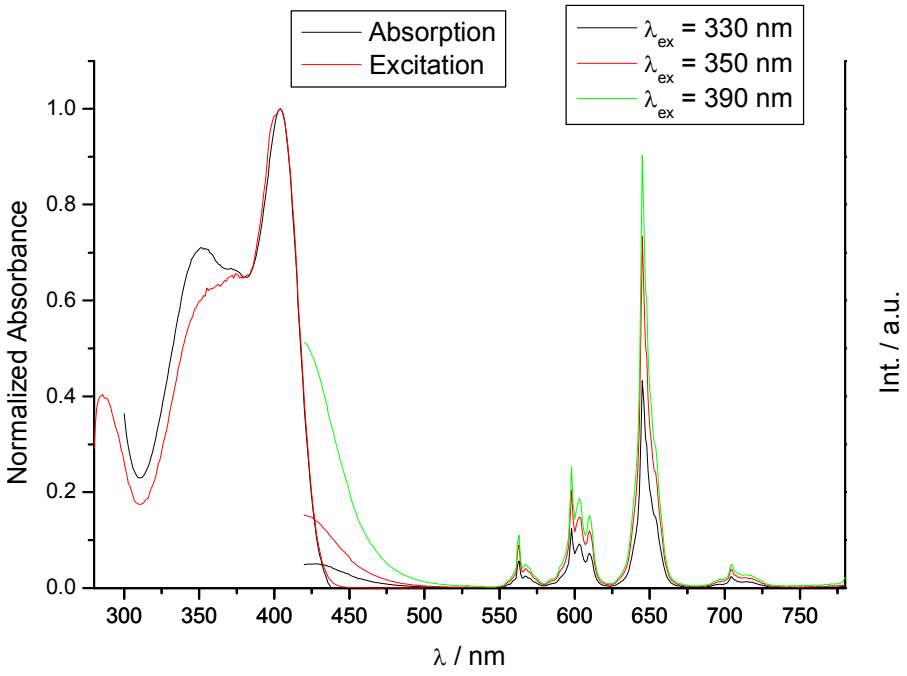


Figure S16 **Sm-2** in benzene.

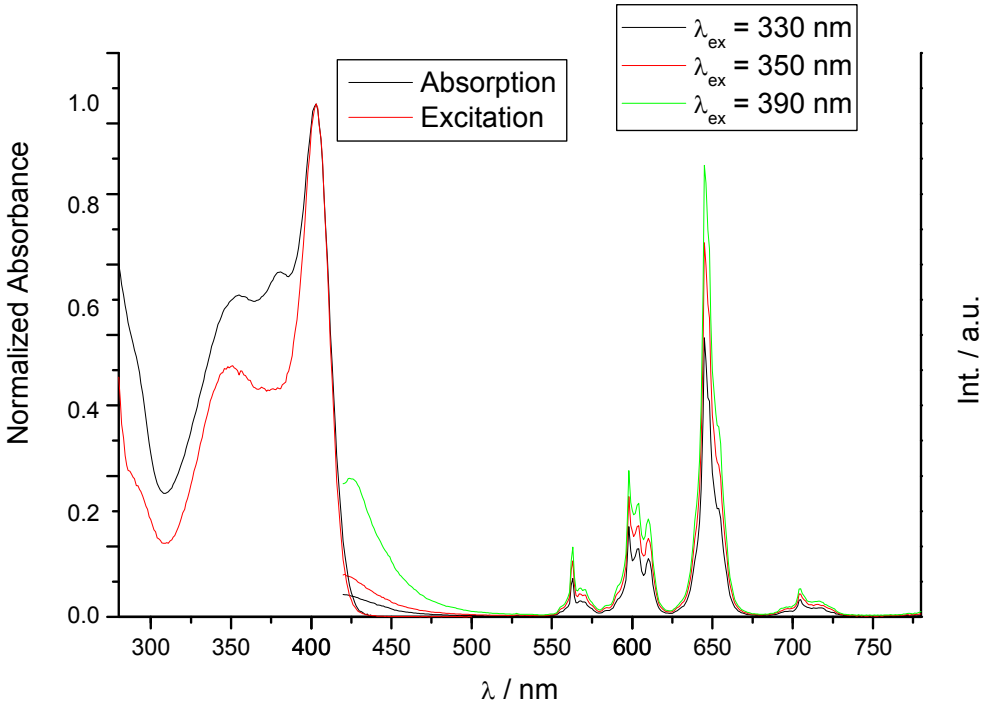


Figure S17 **Sm-2** in carbon tetrachloride.

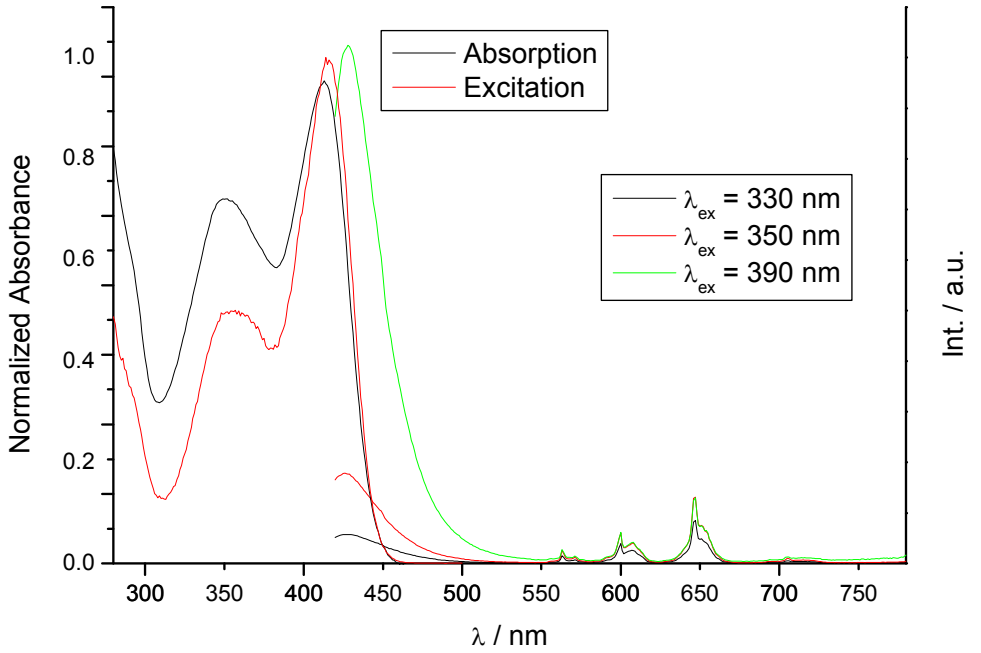


Figure S18 **Sm-2** in chloroform.

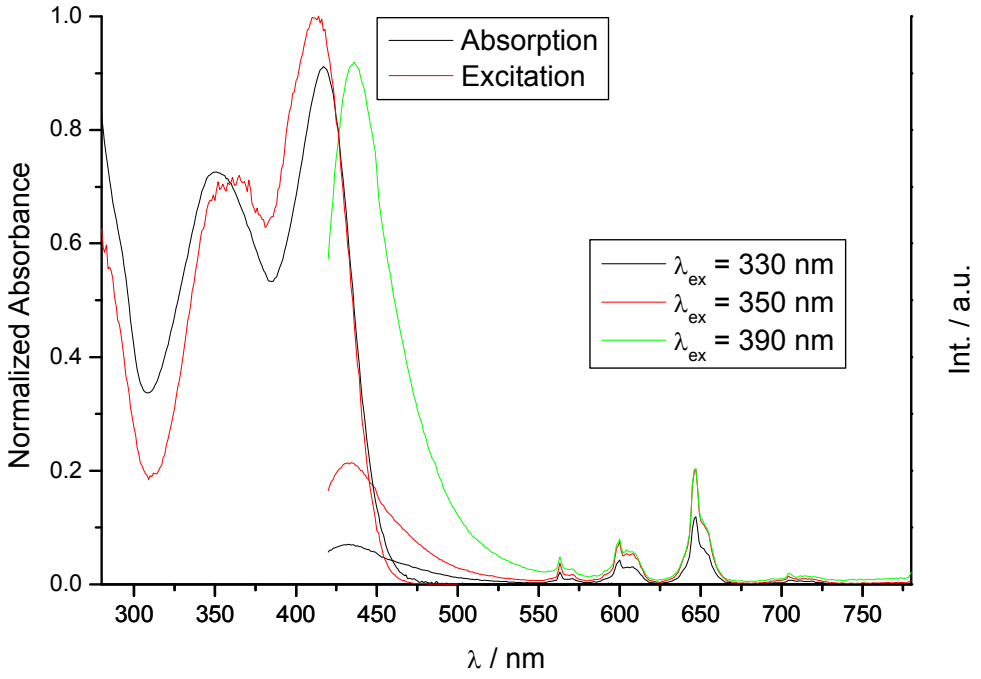


Figure S19 **Sm-2** in dichloromethane.

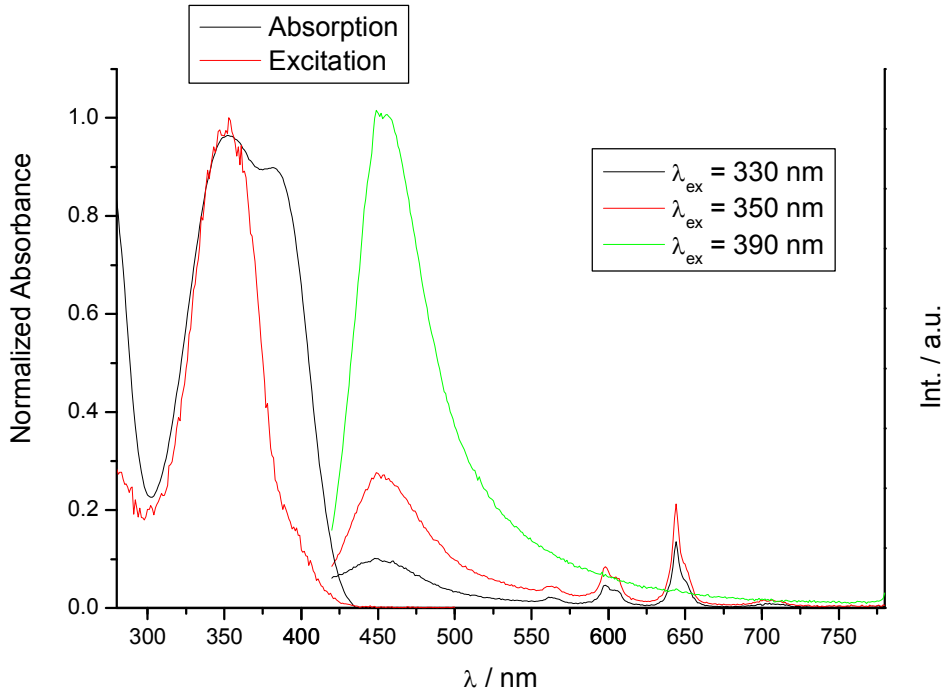


Figure S20 **Sm-2** in dimethyl sulfoxide.

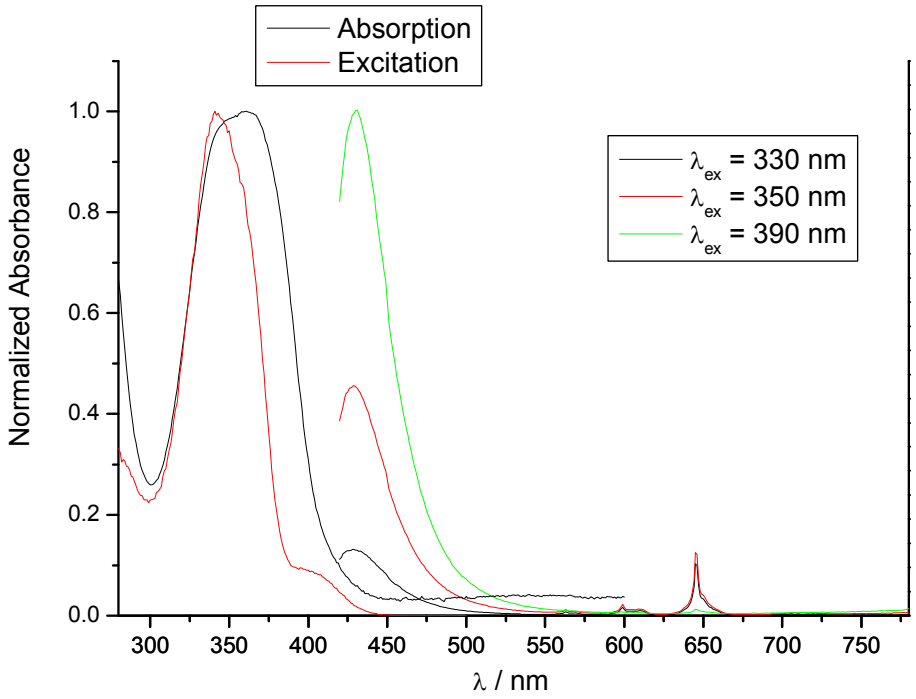


Figure S21 **Sm-2** in ethyl acetate.

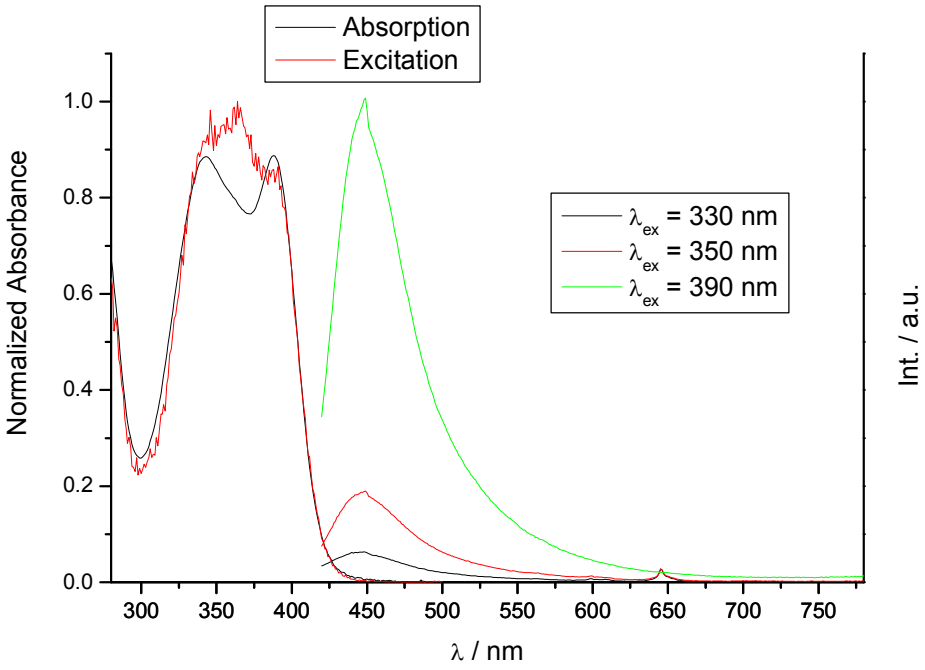


Figure S22 **Sm-2** in isopropanol.

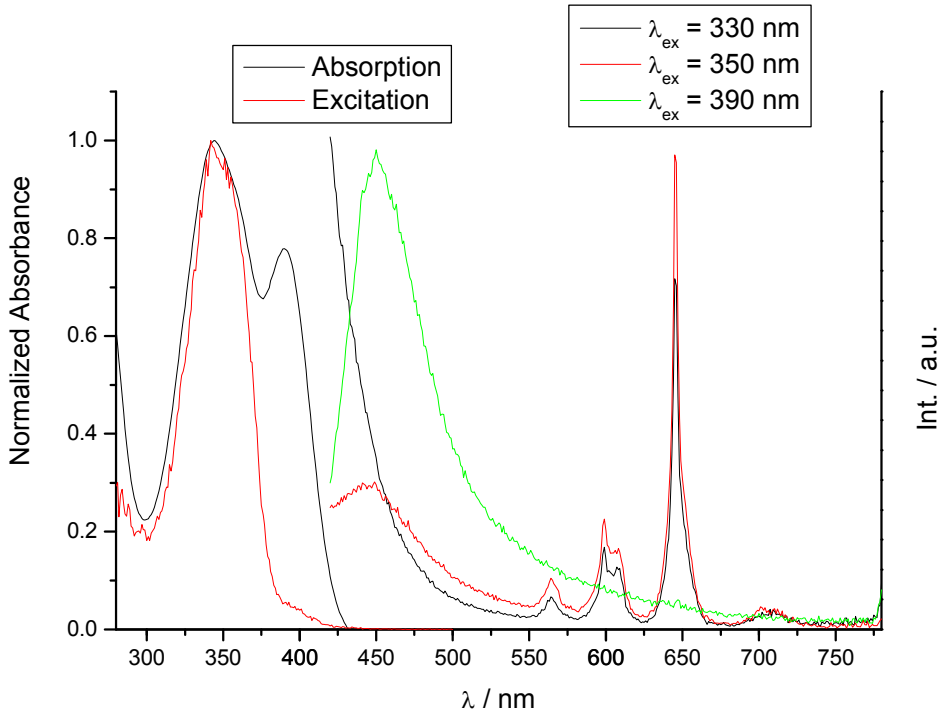


Figure S23 **Sm-2** in methanol.

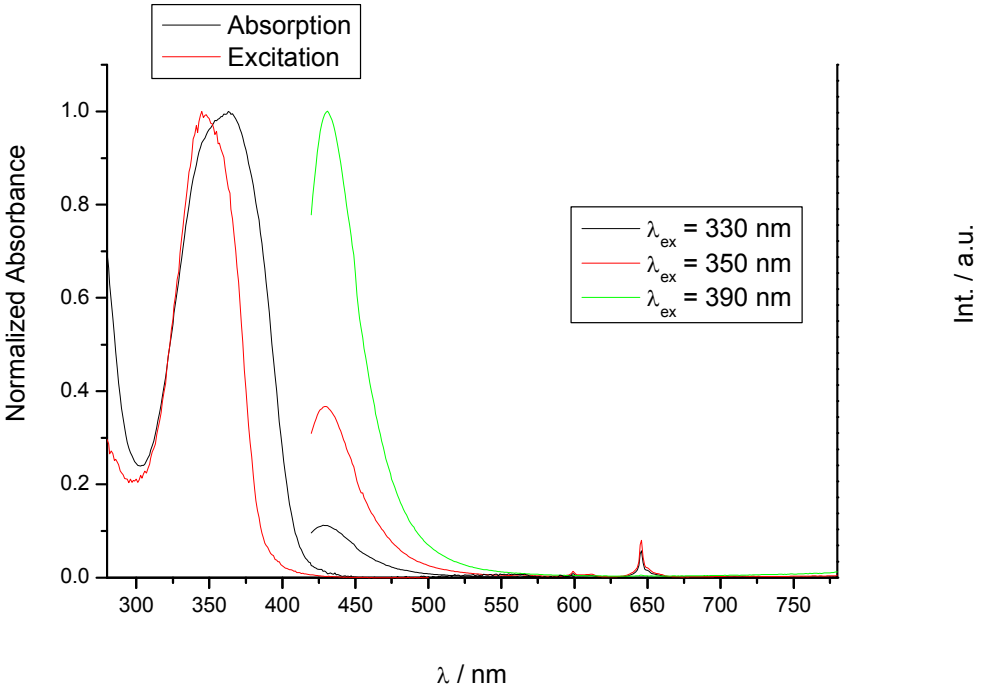


Figure S24 **Sm-2** in tetrahydrofuran.

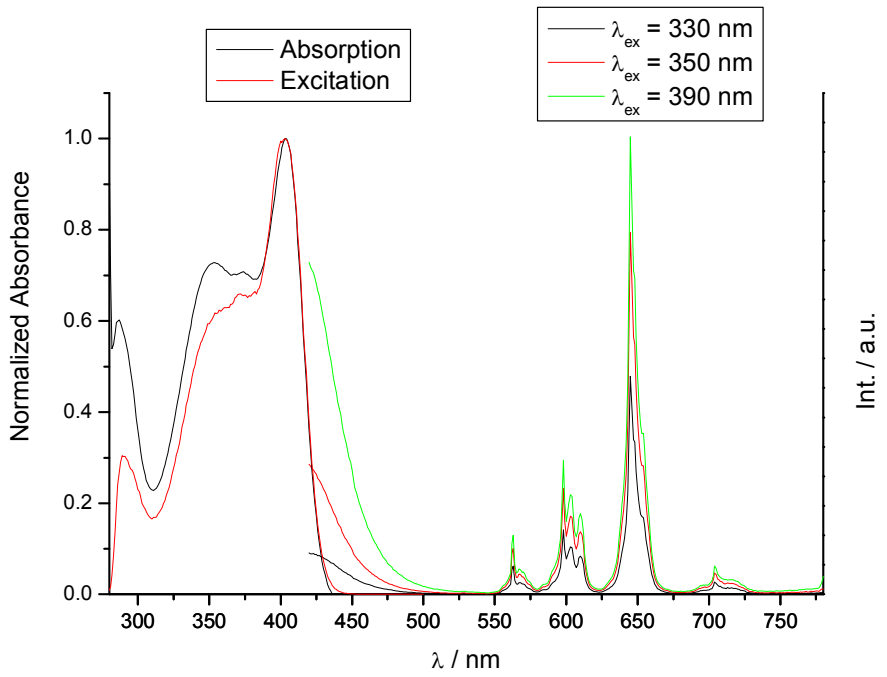


Figure S25 **Sm-2** in toluene.

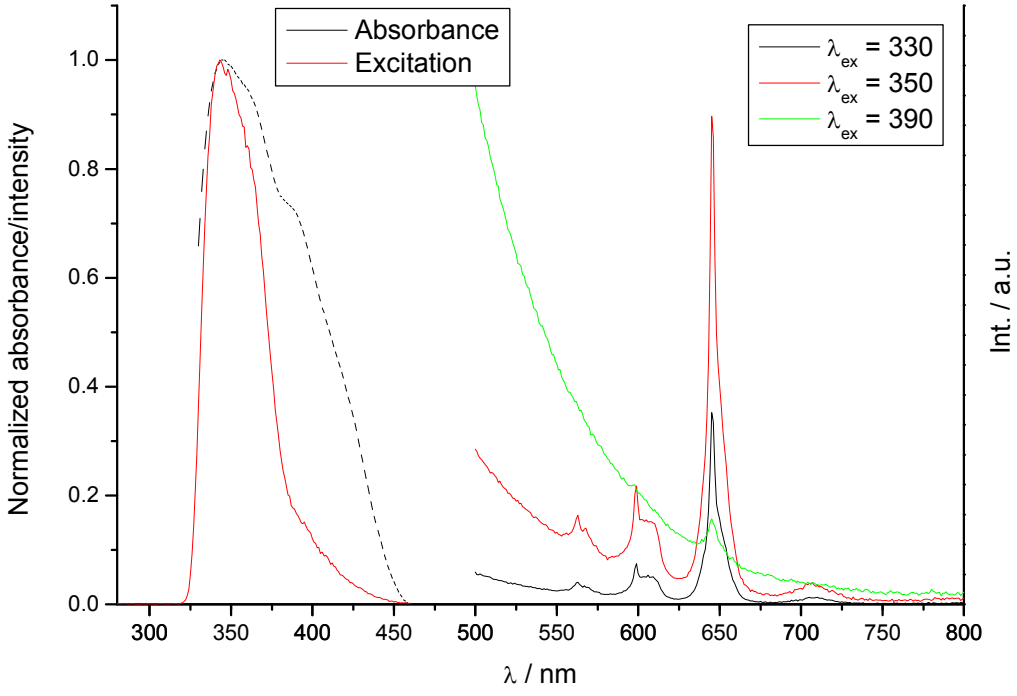


Figure S26 **Sm-3** in acetone.

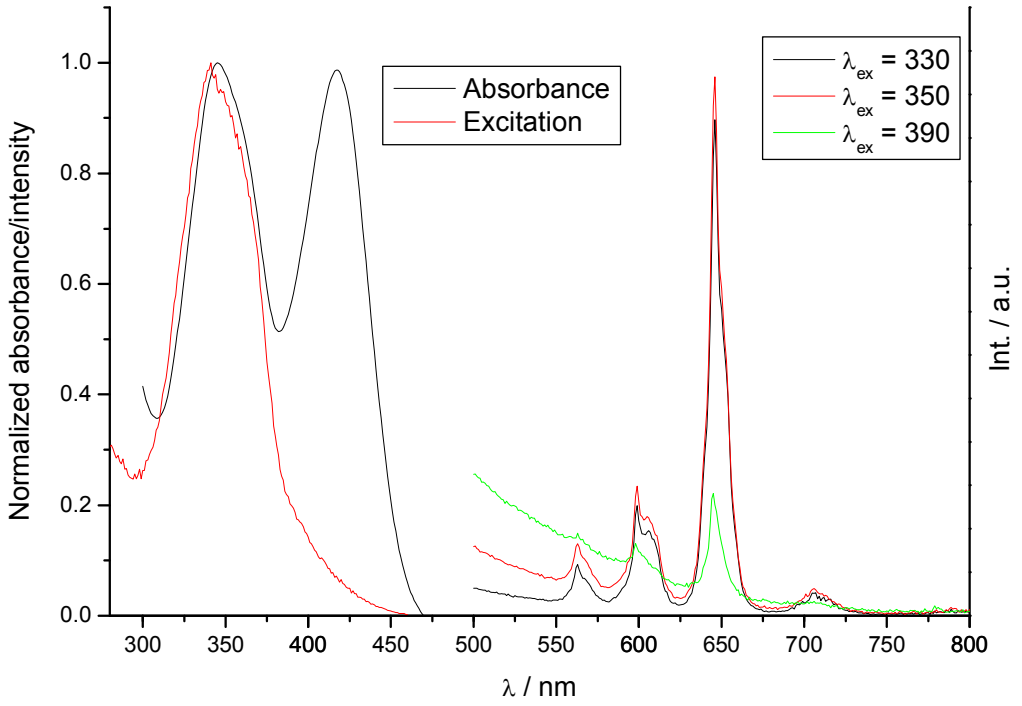


Figure S27 **Sm-3** in acetonitrile.

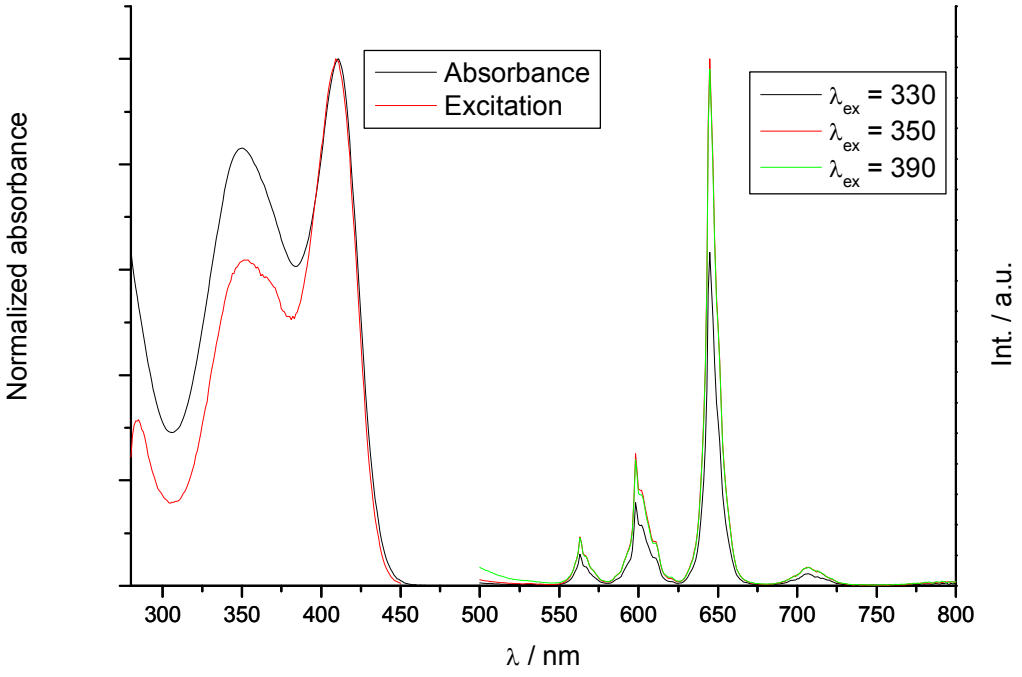


Figure S28 **Sm-3** in benzene.

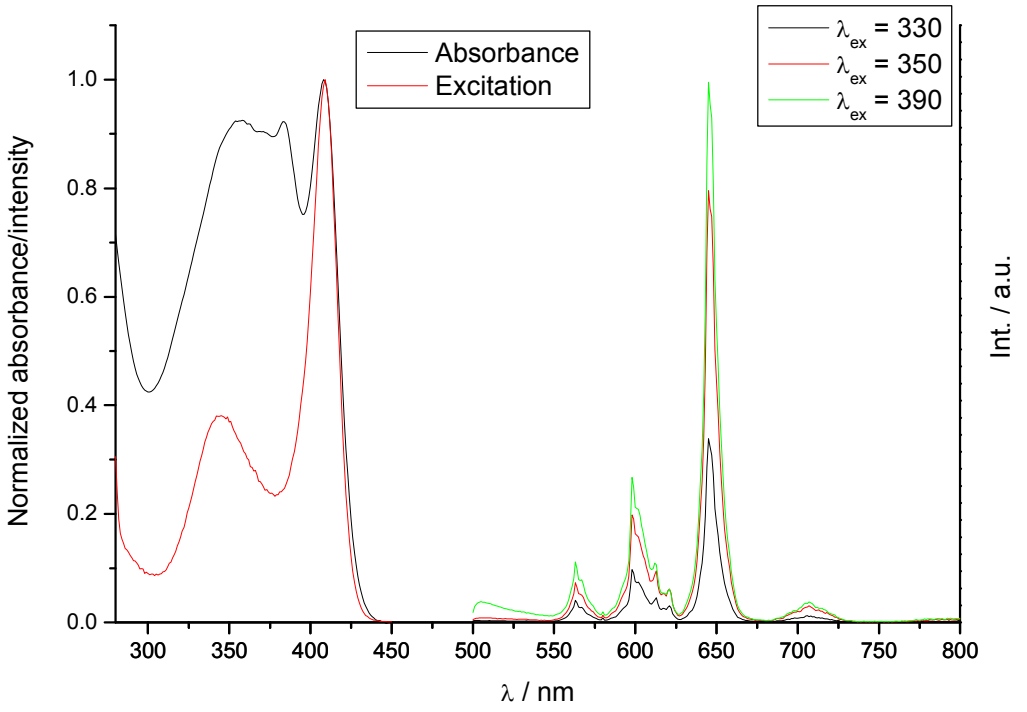


Figure S29 **Sm-3** in carbon tetrachloride.

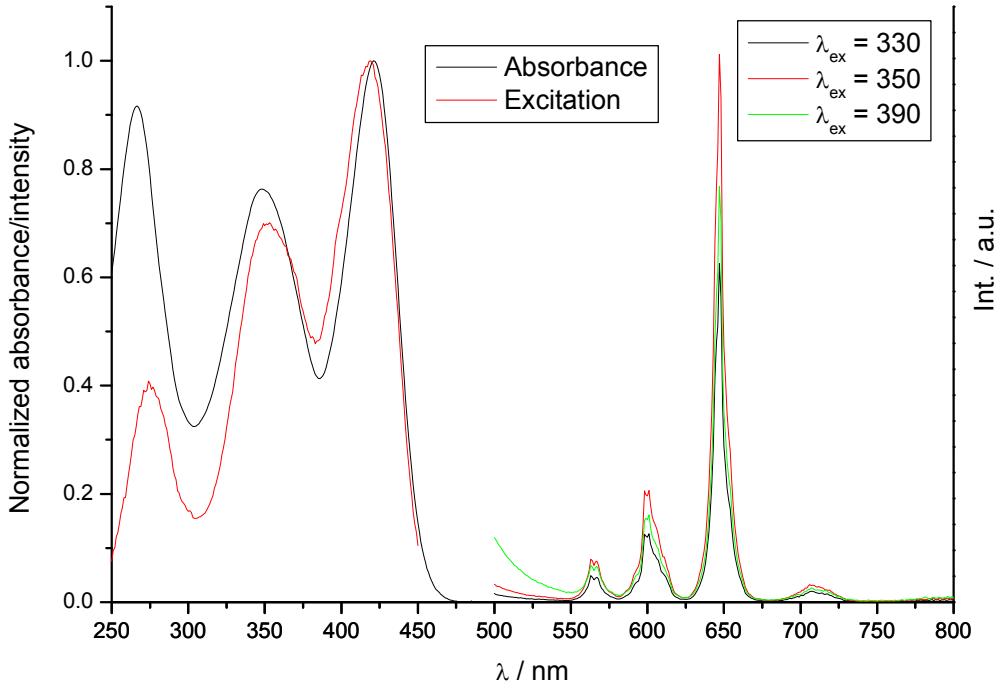


Figure S30 **Sm-3** in chloroform.

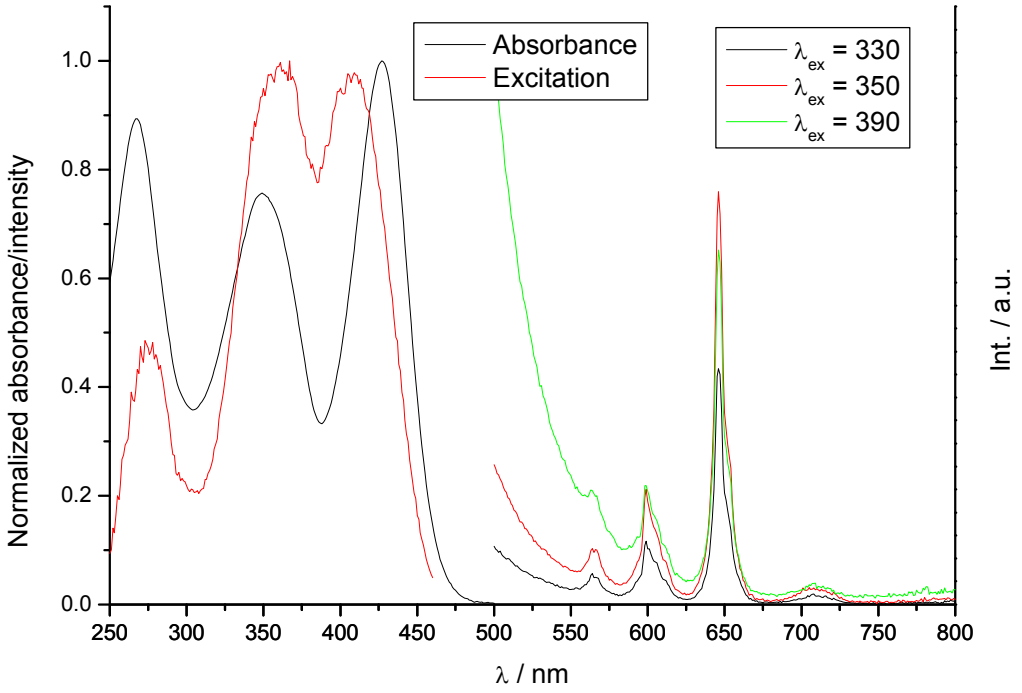


Figure S31 **Sm-3** in dichloromethane.

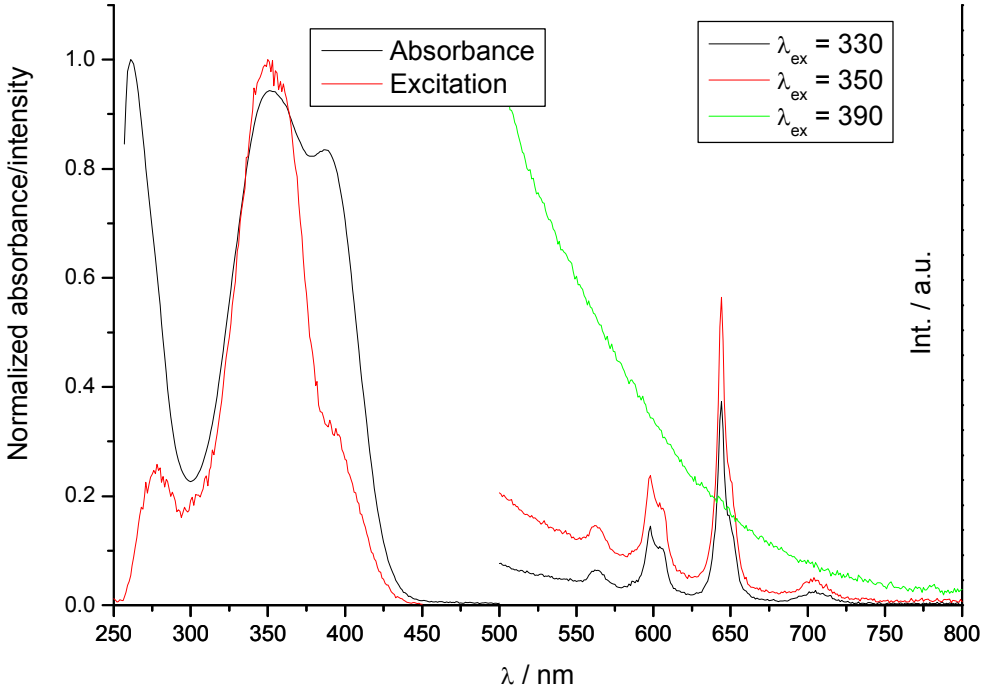


Figure S32 **Sm-3** in dimethyl sulfoxide.

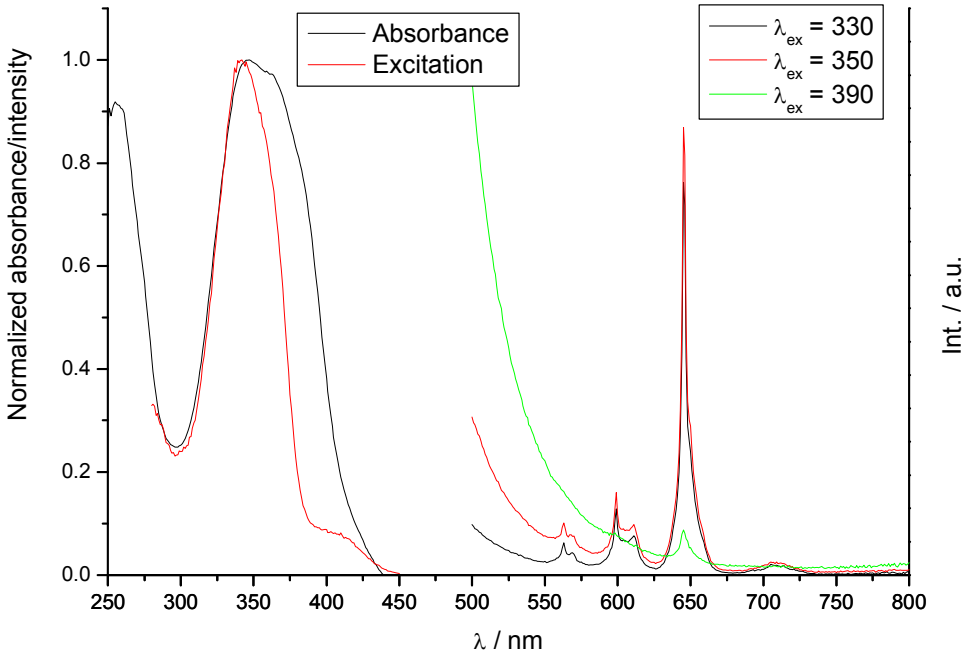


Figure S33 **Sm-3** in ethyl acetate.

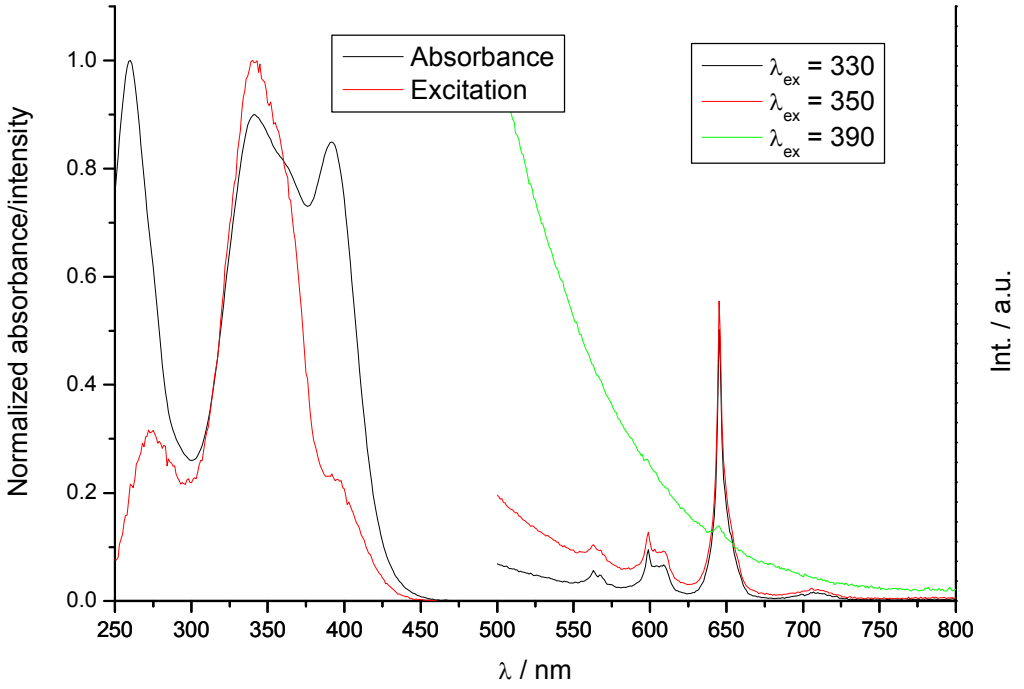


Figure S34 **Sm-3** in isopropanol.

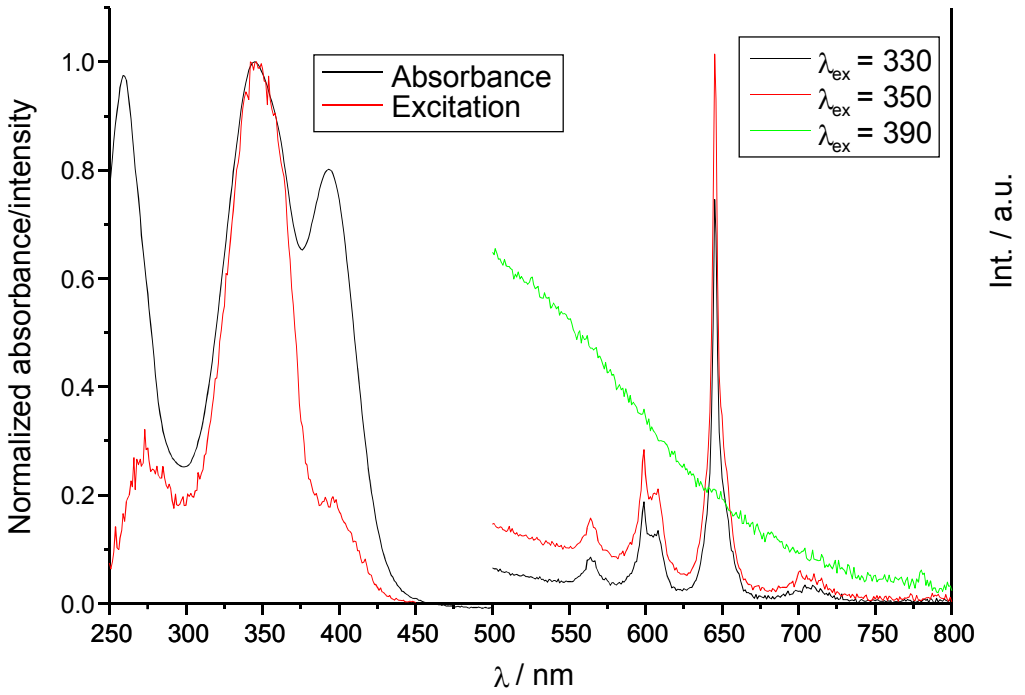


Figure S35 **Sm-3** in methanol.

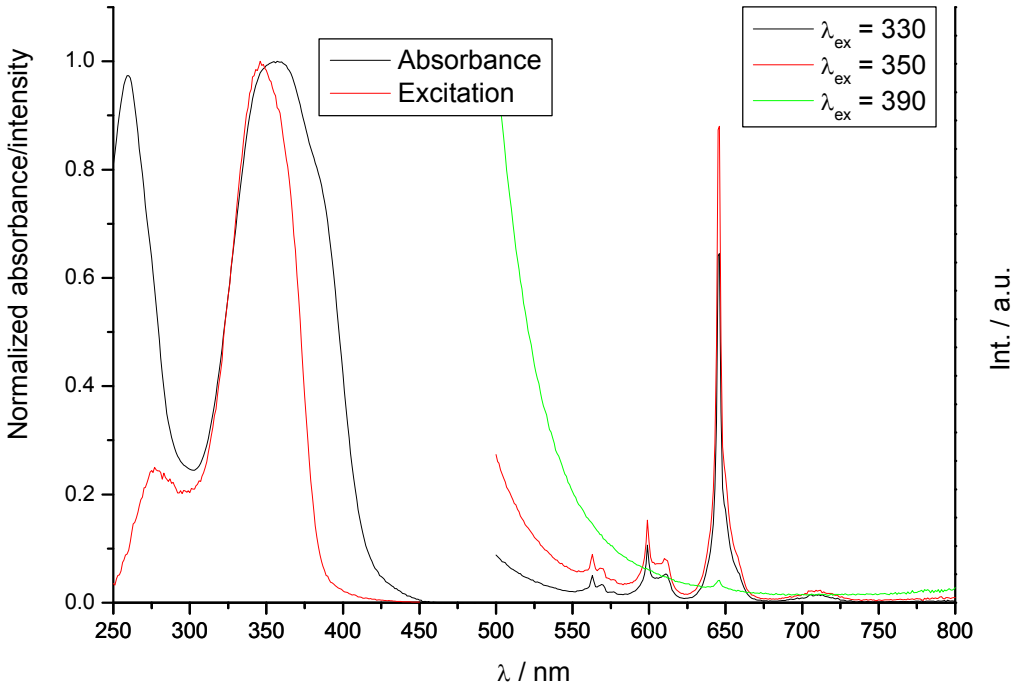


Figure S36 **Sm-3** in tetrahydrofuran

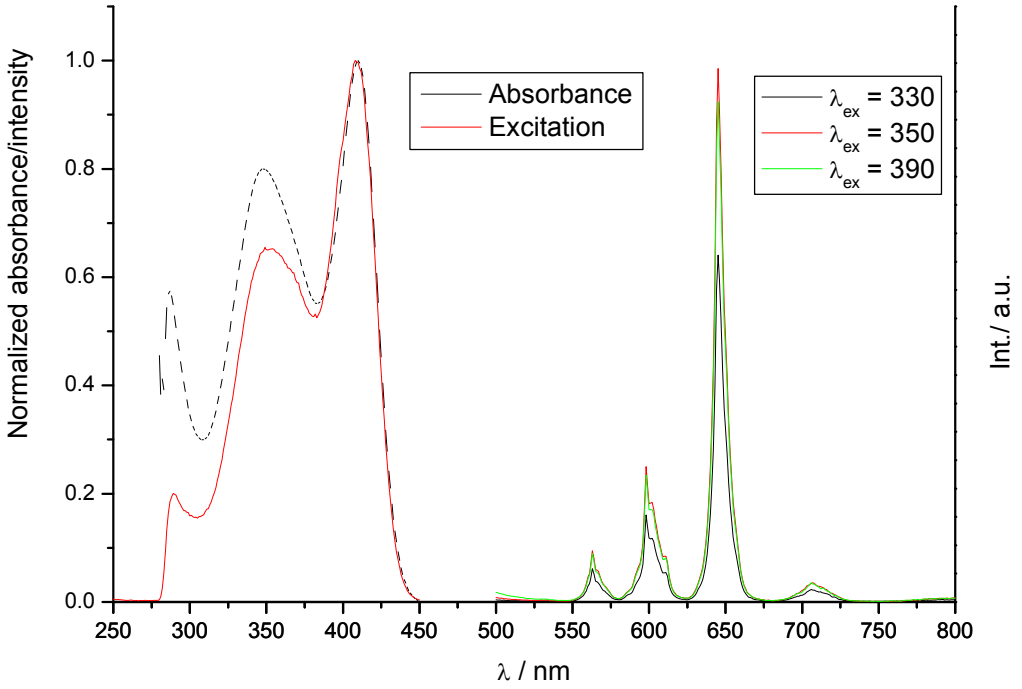


Figure S37 **Sm-3** in toluene.

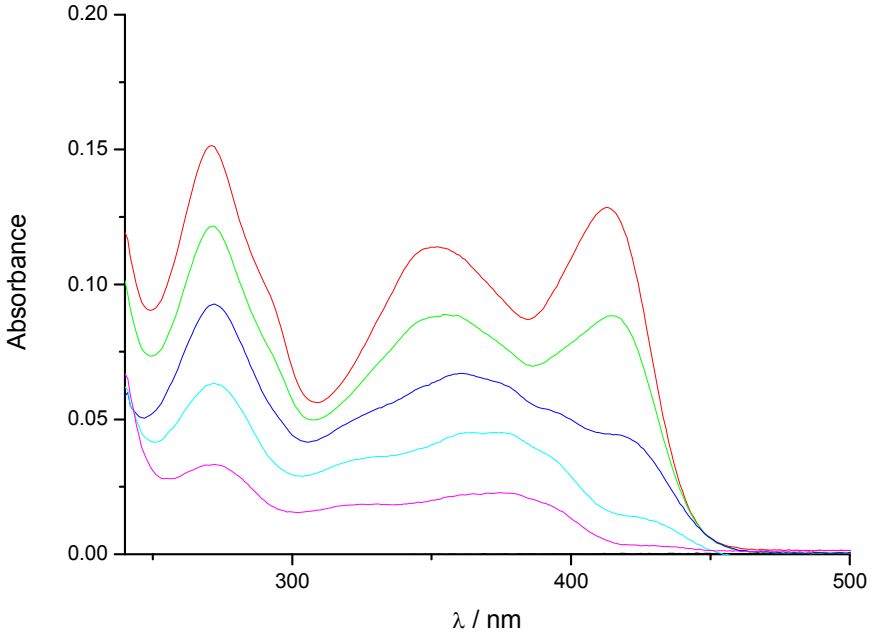


Figure S38 UV-vis absorption spectrum of **Sm-1** in successive $CHCl_3$ dilutions, showing deterioration of ILCT band and possible appearance of free ligand absorption peak merged with absorption of tta.

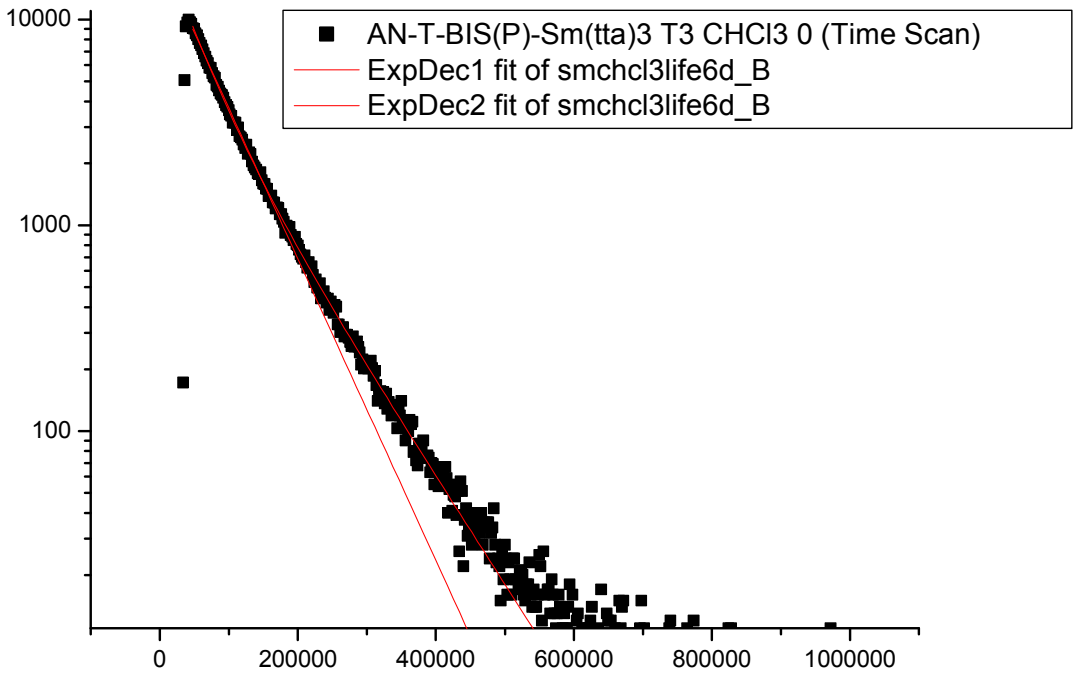


Figure S39 Biexponential luminescence decay curve of **Sm**-**3** in CHCl3.

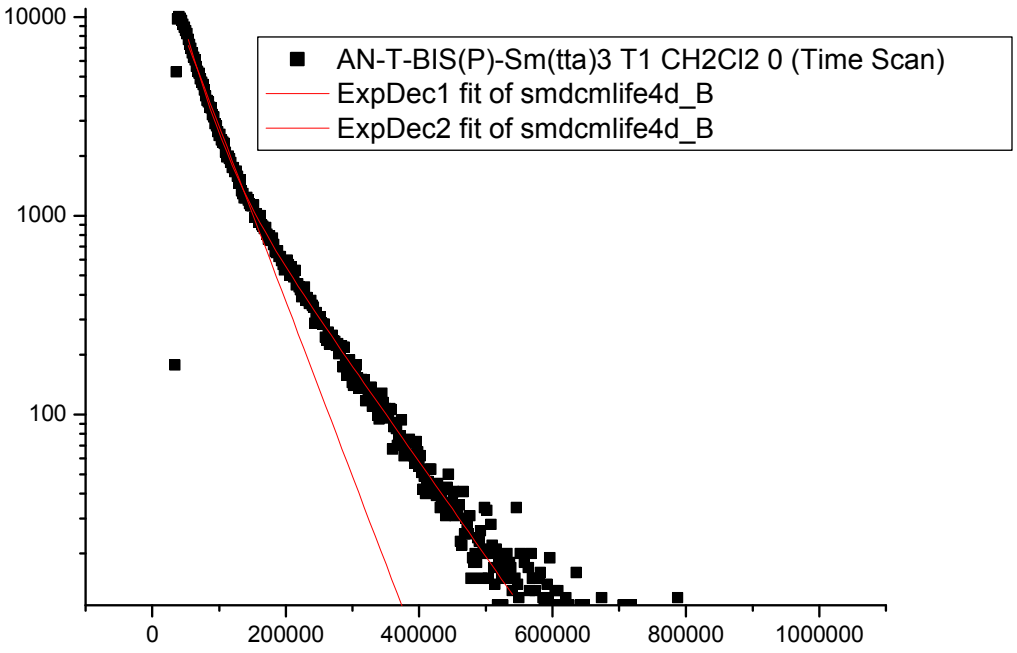


Figure S40 Biexponential luminescence decay curve of **Sm-3** in CH_2Cl_3.

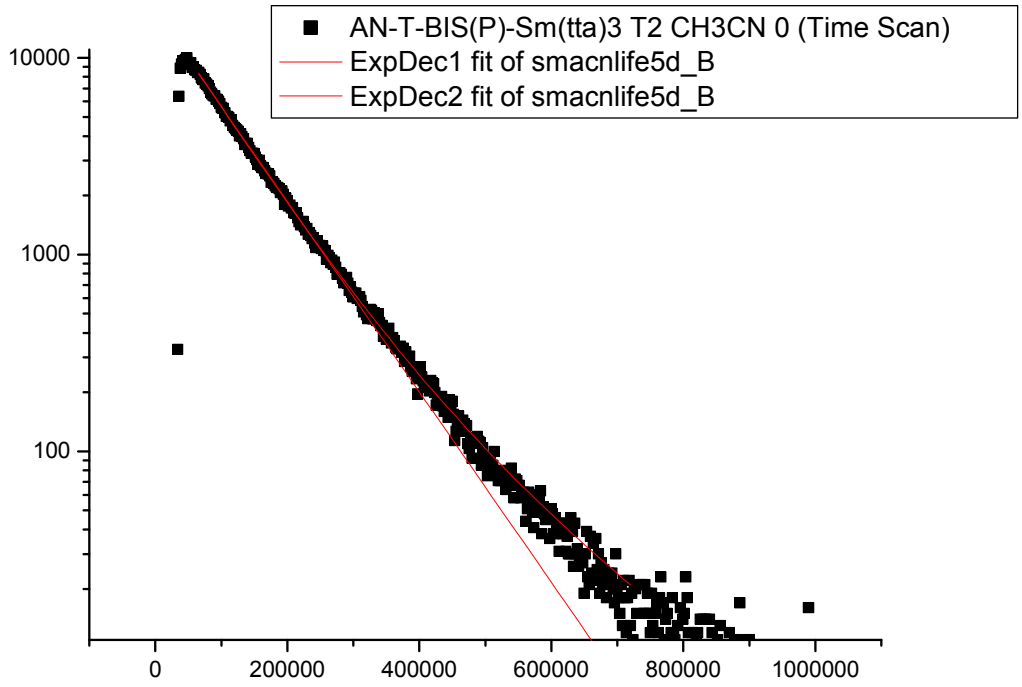


Figure S41 Biexponential luminescence decay curve of **Sm-3** in CH_3CN.

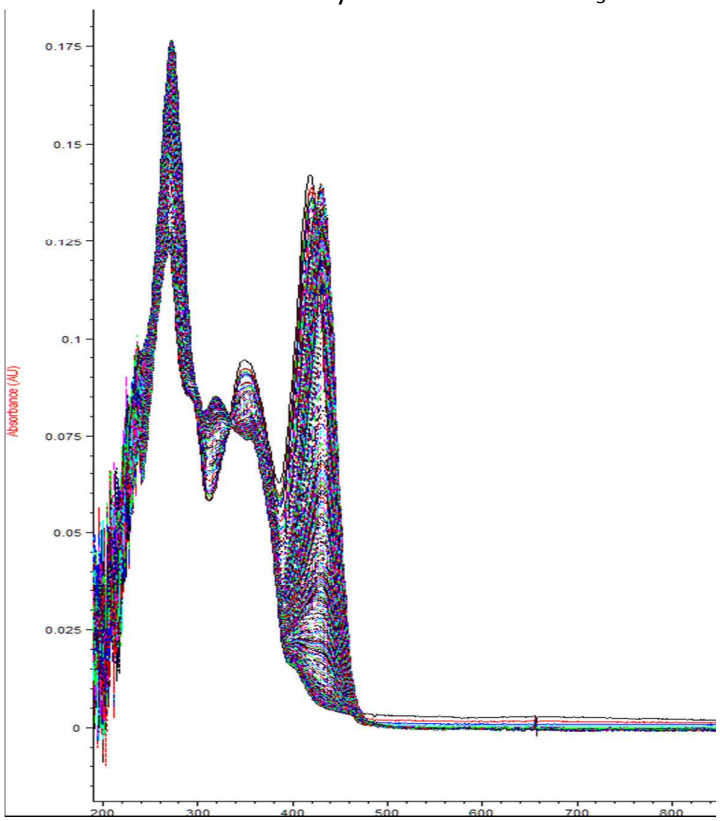


Figure S42 UV-absorption spectrum of **Sm**-**1** in $CHCl_3$ over 3 hours, spectrum taken every 30s.

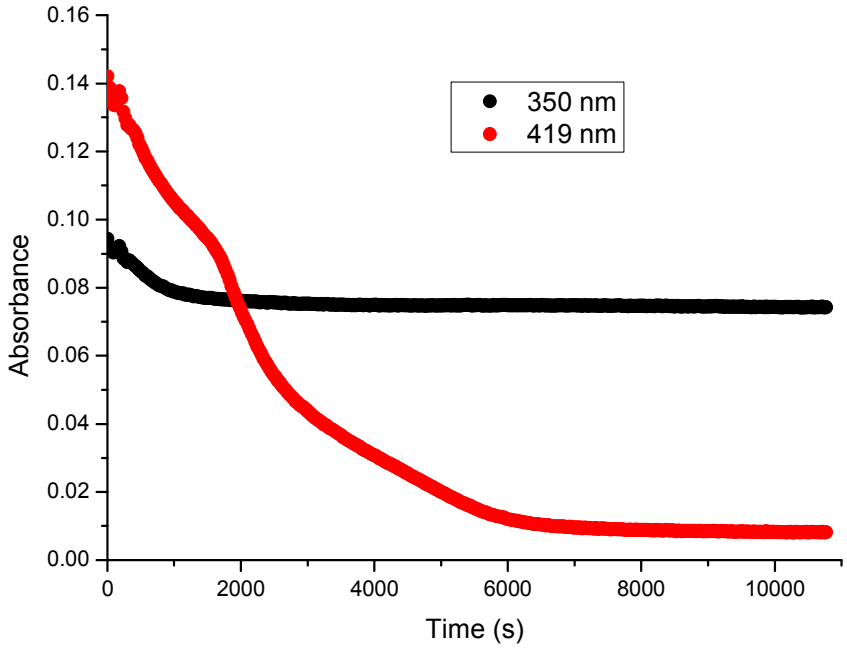


Figure S43 Spectra showing the change in absorbance of peaks 350 nm and 419 nm of **Sm-1** in $CHCl_3$ over 3 hours

Solvent	Lifetime (μs), (*q*)		
	Sm-1	**Sm-2**	**Sm-3**
Benzene	114	113	106
Benzene-d6	103	127	124
$CHCl_3$	66.3	64	27.2
$CDCl_3$	76.7	95.4	85.6
CH_2Cl_2	27.8	26.8	22.4
CD_2Cl_2	40.1	47.4	26.9
CH_3OH	12.7	12.3	15.9
CD_3OD	132 (3.6)	132 (3.7)	131 (2.8)
CH_3CN	71.2	88.5	55.5
CD_3CN	84.8	95.0	73.1

Table S1 Luminescence lifetimes in the visible region for **Sm-1-3** in selected solvents and the deuterated solvent.