Electronic Supplementary Material (ESI) for ChemComm.

Disaggregation of sumanene-containing fluorescent probe towards highly sensitive and specific detection of caesium cation

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Electronic Supplementary Information (ESI)

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S1. Experimental section

S1.1 Materials and methods

Chemical reagents and solvents were commercially purchased and purified according to the standard methods, if necessary. The NMR experiments were carried out using a Varian VNMRS 500 MHz spectrometer (^{1}H NMR at 500 MHz or ^{13}C NMR at 125 MHz) equipped with a multinuclear z-gradient inverse probe head. Unless otherwise stated, the spectra were recorded at 25 °C. Standard 5 mm NMR tubes were used. ^{1}H and ^{13}C chemical shifts (δ) were reported in parts per million (ppm) relative to the solvent signal: $CDCl_3$, δ_H (residual $CHCl_3$) 7.26 ppm, δ_C 77.2 ppm. NMR spectra were analyzed with the MestReNova v12.0 software (Mestrelab Research S.L). UV-Vis and PL measurements were performed with a Cytation 3 Cell Multi-Mode Reader (BioTek Instruments, Inc.) with the spectral resolution of 1 nm. For the UV-Vis and PL measurements, the wavelengths for the absorption or emission maxima λ_{max} were reported in nm. TOF-HRMS (ESI) measurements were performed with a Q-Exactive ThermoScientific spectrometer. Melting point was determined on Standford Research Systems MPA 100 and was uncorrected. Dynamic light scattering (DLS) measurements were performed using Malvern Zetasizer instrument. Elemental analyses were performed using CHNS Elementar Vario EL III apparatus. Each elemental composition was reported as an average of two analyses. TLC analysis was performed using Merck Silica gel 60 F254 plates.

3,5-Diphenylbromobenzene[1] and sumanene[2] were prepared following the literature procedures.

S1.2 Synthesis of 1-(4-formylphenyl)-3,5-diphenylbenzene (3)

Phenylboronic acid (100.0 mg, 0.358 mmol, 110 mol%), 3,5-diphenylbromobenzene (54.0 mg, 0.325 mmol, 100 mol%), $Pd(PPh_3)_4$ (40 mg, 0.033 mmol, 10 mol%) and 2M Na_2CO_3 (0.5 mL) were refluxed in dry THF (5 mL) under argon atmosphere for 12 hours. Distilled water (5 mL) was added. Water layer was extracted with $CHCl_3$ (3x25 mL). The organic layers were combined, washed with brine (3 mL), dried with $MgSO_4$, filtered, and the solvent was removed in vacuum. The resultant residue was purified by column chromatography (SiO_2; 40% hex/CH_2Cl_2) to give 1-(4-formylphenyl)-3,5-diphenylbenzene (**3**; 84.7 mg, 78% yield) as the white solid.

The NMR data are consistent with the literature.[3]
^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ_H 10,09 (s, 1H), 8.01-7.99 (m, 2H), 7.89-7.85 (m, 3H), 7.82-7.81 (m, 2H), 7.72-7.70 (m, 4H), 7.52-7.49 (m, 4H), 7.43-7.40 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, ppm), δ_C 192.1, 147.3, 142.8, 141.1, 141.0, 135.6, 130.5, 129.1, 128.1, 128.0, 127.5, 126.5, 125.4; TOF-HRMS (ESI): calcd. for $C_{25}H_{19}O$ $[M+H]^+$ = 335.1431, found: m/z 335.1429; Elemental analysis: calculated: C, 88.79; H, 5.43; N, 0.00%; found: C, 88.72; H, 5.45; N, 0.00%; R_f (40% hex/CH_2Cl_2) = 0.75.

S1.3 Synthesis of sumanene derivative 5

Sumanene (**4**; 10.0 mg, 0.038 mmol, 100 mol%) and Bu_4NBr (12.0 mg, 0,019 mmol, 50 mol%) were added to a test tube. The reaction flask was purged with argon. Dry THF (0.3 mL) and 30% $NaOH_{aq}$ (2 mL in degassed water) were added. The reaction mixture was stirred for 5 minutes at 27 °C. A solution of 1-(4-formylphenyl)-3,5-diphenylbenzene (**3**; 63.5 mg, 0.19 mmol, 500 mol%) in dry THF (0.8 mL) was added and the mixture was stirred under argon atmosphere at 27 °C for 24 hours. Distilled water (6 mL) was added. Water layer was extracted with CH_2Cl_2 (3x20 mL). The organic layers were combined and washed with saturated $NaHCO_3$ (3 mL), brine (3 mL), dried with $MgSO_4$, filtered, and the solvent was removed in vacuum. The resultant residue was purified by PTLC (50% hex/CH_2Cl_2) to give the target sumanene derivative (**5**; 33.6 mg, 73% yield) as the light-orange solid.

Mp: >300 °C; ^{1}H NMR ($CDCl_3$, 500 MHz, ppm), δ_H 8.07-8.03 (m, 3H), 8.00-7.96 (m, 3H), 7.91-7.69 (m, 28H), 7.60-7.57 (m, 1H), 7.53-7.36 (m, 24H), 7.32-7.31 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, ppm), δ_C 147.8, 147.7, 147.5, 147.4, 146.2, 145.8, 145.7, 145.5, 147.7, 142.6, 142.5, 141.7, 141.7, 141.6, 141.6, 141.4, 141.2, 141.1, 141.0, 140.9, 140.7, 135.8, 135.7, 135.6, 132.7, 130.5, 130.4, 129.2, 129.1, 129.0, 128.9, 128.8, 127.8, 127.7, 127.6, 127.5, 127.4, 125.7, 125.6, 125.2, 125.1, 123.9, 123.7, 123.6, 123.4, 121.2, 121.1, 121.0, 120.9; UV-Vis, λ_{max} ($CHCl_3$) 260, 366, 478 nm; HRMS (TOF): calcd. for $C_{96}H_{60}$ $[M]^+$ = 1212.4695, found: m/z 1212.4700; Elemental analysis: calculated: C, 95.02; H, 4.98; N, 0.00%; found: C, 95.05; H, 4.95; N, 0.00%; R_f (50% hex/CH_2Cl_2) = 0.50.

S1.4 Photophysical studies on 5 and Cs^+ recognition assay

The concentration of the samples for UV-Vis and PL analyses was $2 \cdot 10^{-5}$ M.

For the aggregation formation studies, the PL spectra were measured in $CHCl_3$-hex or $CHCl_3$-CH_3OH mixtures with different volume fractions of poor solvent. Stock solution of **5** in $CHCl_3$ was prepared. An aliquot of the stock solution was transferred to a vial. Poor solvent (hex or CH_3OH) was added to furnish $2 \cdot 10^{-5}$ M mixtures in which the poor solvent fraction was 0–95 vol%. These mixtures were intensively shaken (450 rpm) for *ca*. 6 minutes before the measurement.

For the metal recognition studies, the PL spectra were measured in mixtures with 95 vol% of MeOH in the presence of given metal nitrate ($CsNO_3$, $NaNO_3$, $RbNO_3$, $Ba(NO_3)_2$, KNO_3, $Mg(NO_3)_2$ or $LiNO_3$).

The PL experiments were repeated three times to check the reproducibility of the results.

S2. NMR spectra

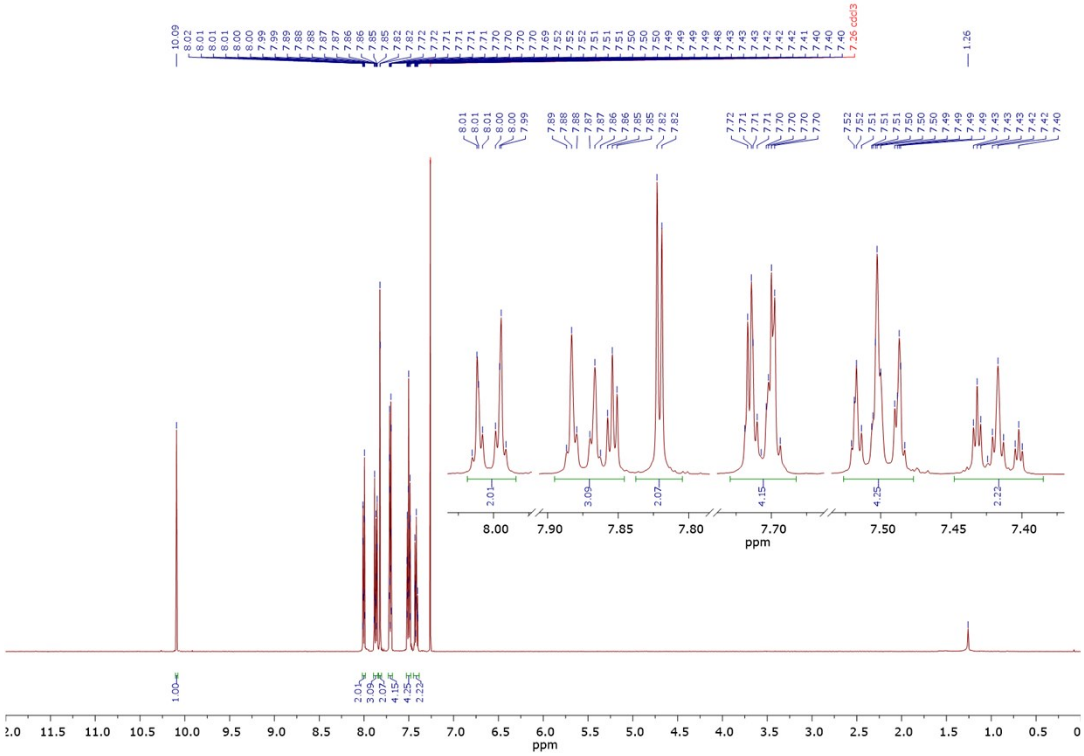

Figure S1. ^{1}H NMR (CDCl$_3$, 500 MHz) spectrum of 1-(4-formylphenyl)-3,5-diphenylbenzene **(3)**.

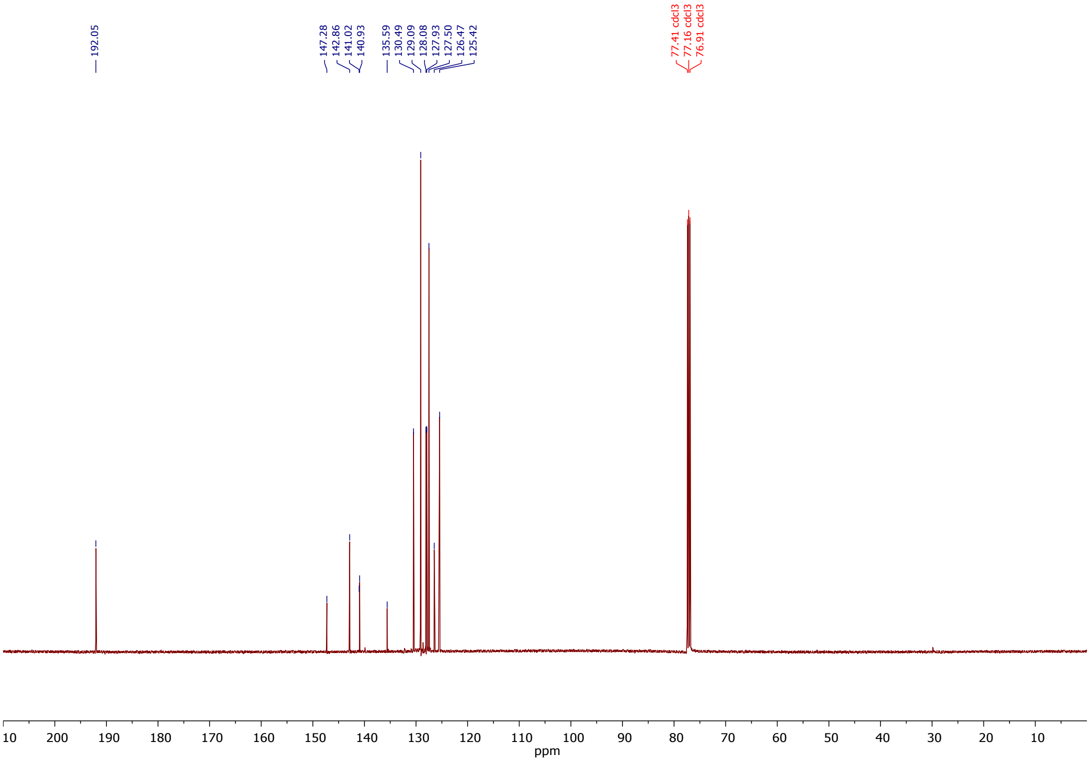

Figure S2. ^{13}C NMR (CDCl$_3$, 125 MHz) spectrum of 1-(4-formylphenyl)-3,5-diphenylbenzene **(3)**.

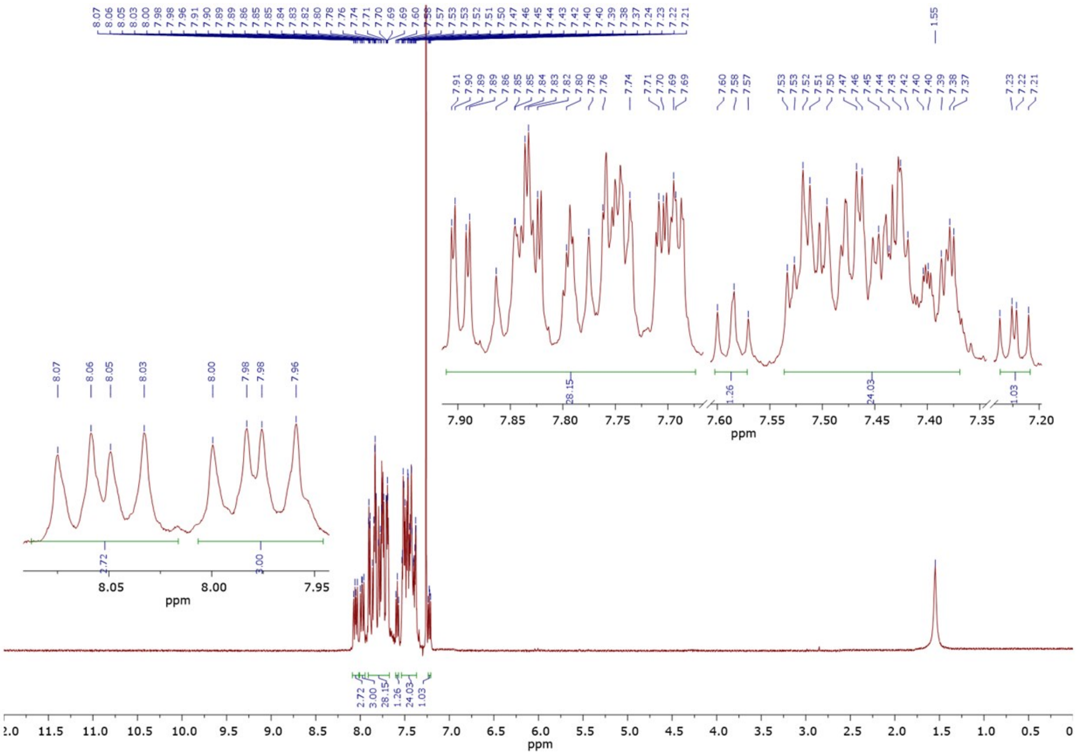

Figure S3. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of sumanene derivative **5**.

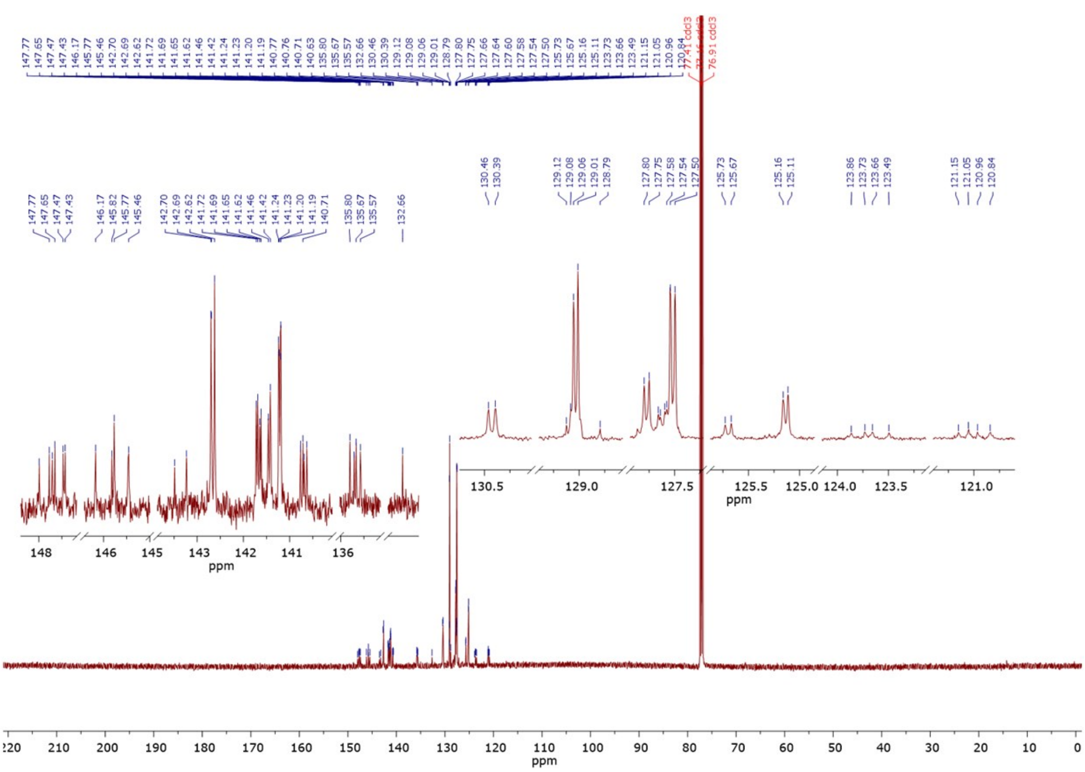

Figure S4. ^{13}C NMR ($CDCl_3$, 125 MHz) spectrum of sumanene derivative **5**.

S3. Emission spectra

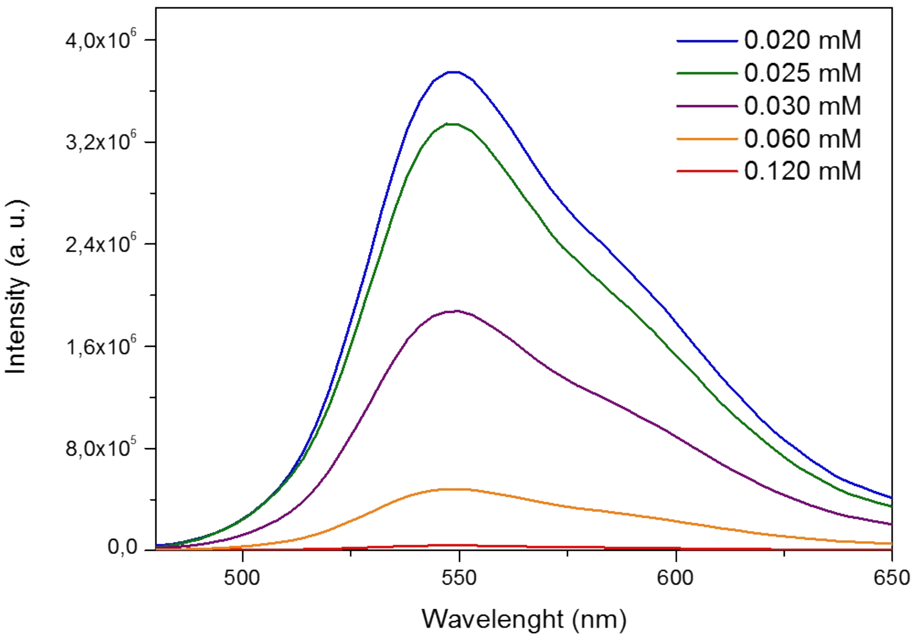

Figure S5. Concentration dependent emission spectra of **3** ($CHCl_3$, $2\cdot10^{-5}$ M; λ_{ex} = 360 nm).

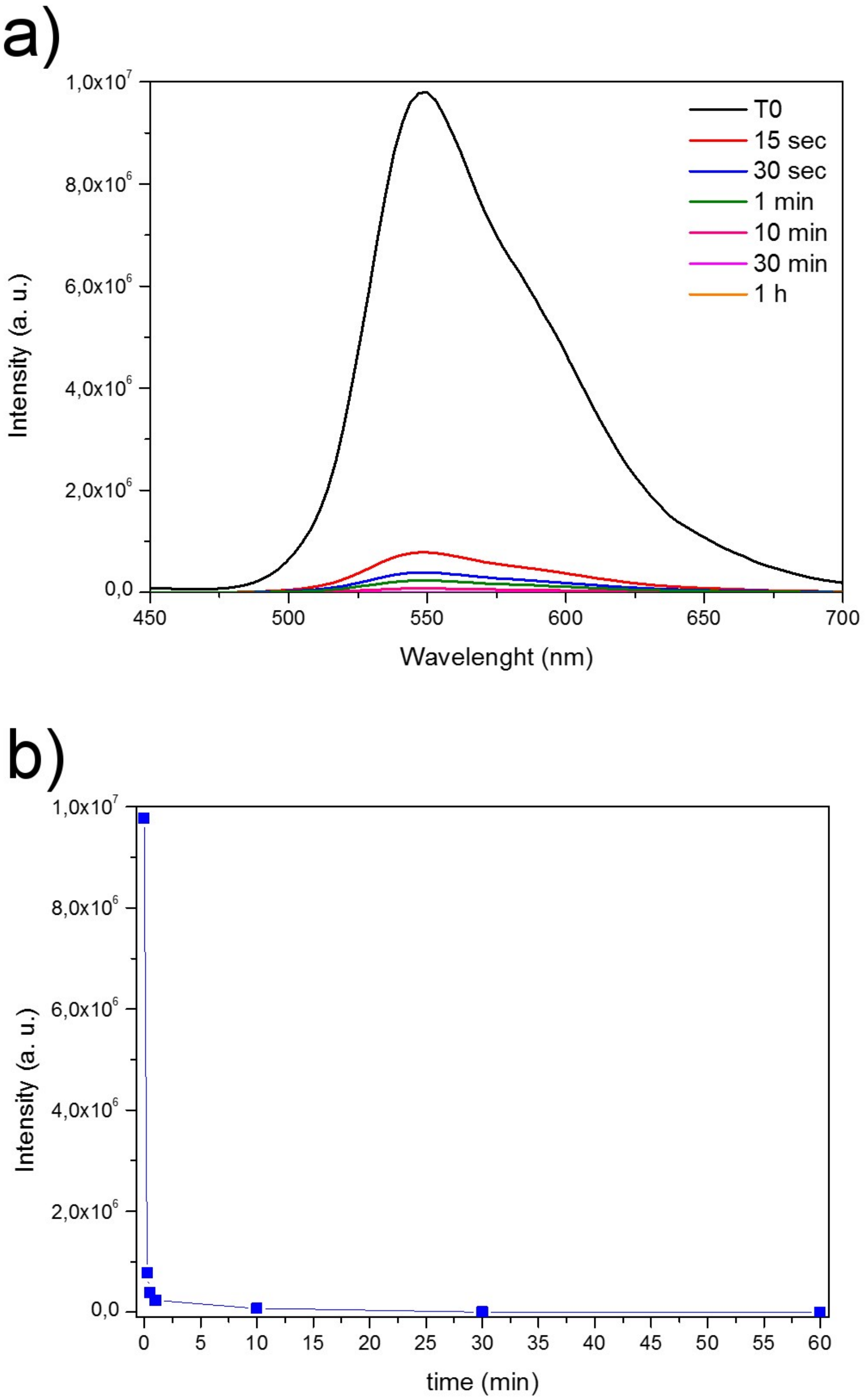

Figure S6. (**a**) Emission spectra of **5** (λ_{ex} = 360 nm) measured in different $CHCl_3$-hex compositions; (**b**) Changes in the emission intensity (λ_{em} = 548 nm) for the samples with different vol% of poor solvent (hex). For (**a**) the annotation stands for the volumetric ratio of poor solvent in each mixture. Black dotted lines in (**a**) indicate the emission spectrum for lyophilized aggregates. For (**b**) error bars are also shown. Concentration of the samples: $2 \cdot 10^{-5}$ M.

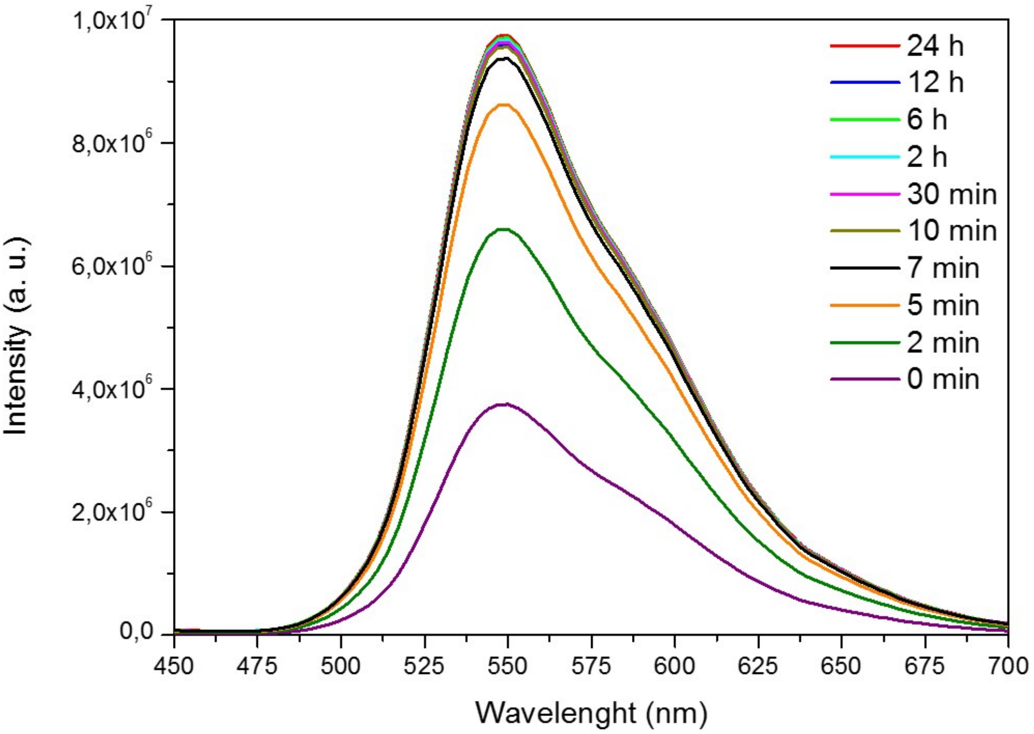

Figure S7. Time-dependent emission intensity change of the aggregated compound (95 vol% CH_3OH in $CHCl_3$; $2 \cdot 10^{-5}$ M; λ_{ex} = 360 nm).

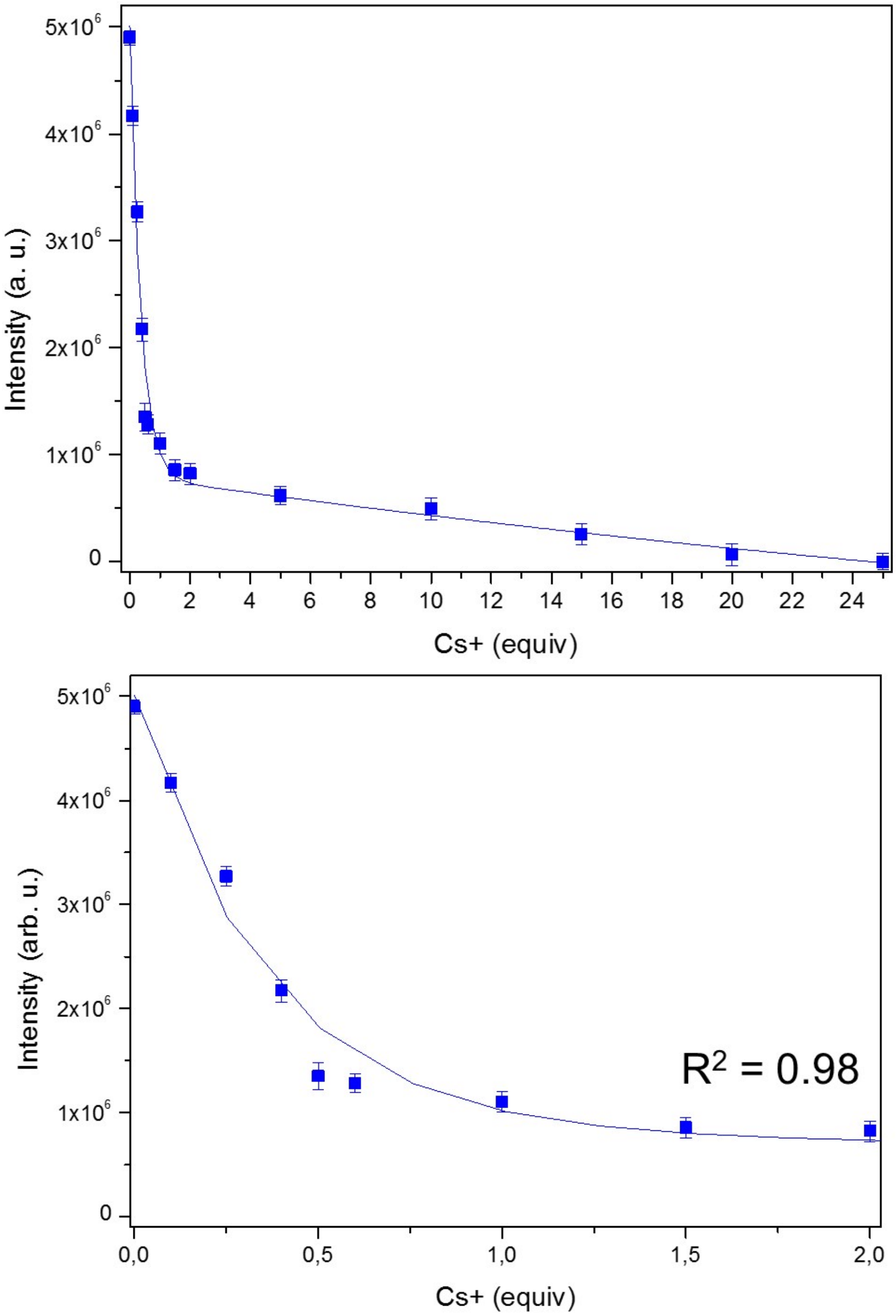

Figure S8. Changes in the emission intensity (λ_{em} = 548 nm) for the samples comprising various amounts (equiv) of Cs^+. The inset of the graph is also presented (bottom).

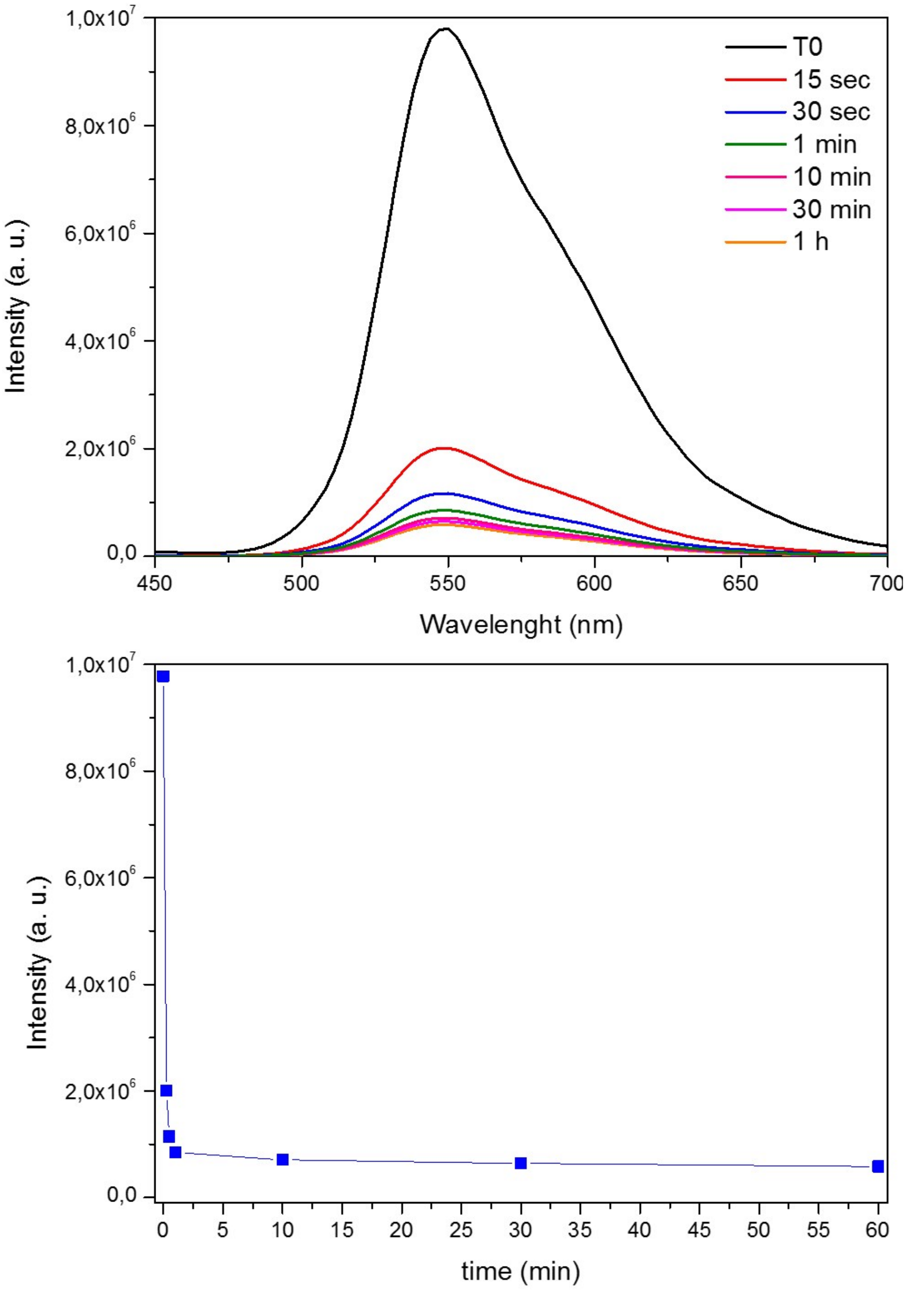

Figure S9. **(Top)** Time-course emission spectra of aggregated **5** (λ_{ex} = 360 nm) in the presence 2 equiv of Cs^+. Concentration of the sample: $2\cdot10^{-5}$ M.; **(Bottom)** Changes in the emission intensity (λ_{em} = 548 nm) for the time-course emission studies with 2 equiv of Cs^+. Concentration of the sample: $2\cdot10^{-5}$ M.

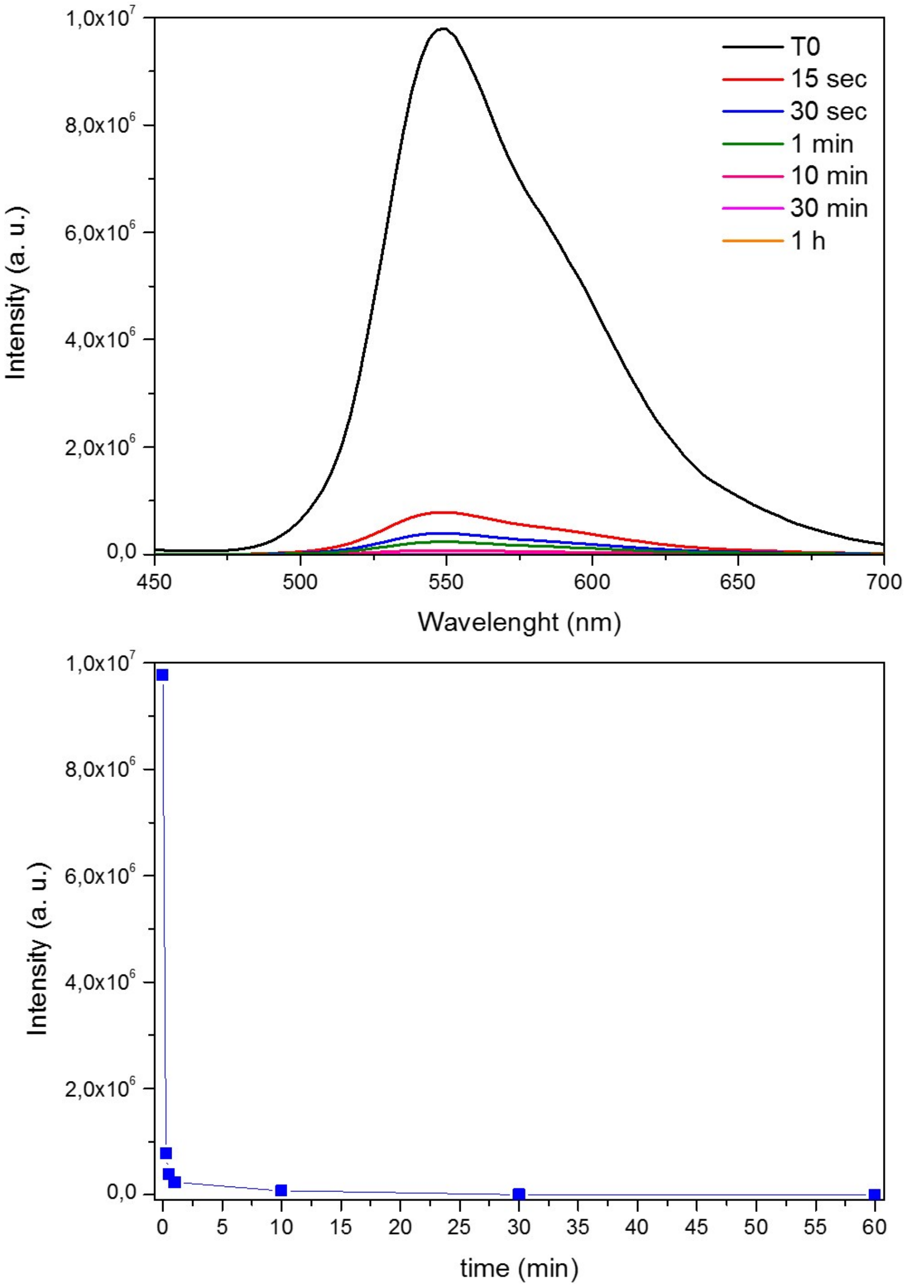

Figure S10. **(Top)** Time-course emission spectra of aggregated **5** (λ_{ex} = 360 nm) in the presence 25 equiv of Cs^+; (**Bottom**) Changes in the emission intensity (λ_{em} = 548 nm) for the time-course emission studies. Concentration of the sample: $2 \cdot 10^{-5}$ M.

S4. Estimation of the emission quantum yields regarding AIEE studies

Emission quantum yields (Φ_E) were estimated using a relative method.[4] The concentration of the samples was $1 \cdot 10^{-6}$ M. Excitation wavelength was 360 nm. Experiments were performed at room temperature. Rhodamine 6G was used as a standard.[5] The following equation was applied for the calculation of Φ_E[4]:

$$\Phi\mathrm{E} = \Phi_s \frac{\int I(\tilde{v})d\tilde{v} \; 1 - e^{-A_s} n^2}{\int I_s(\tilde{v})d\tilde{v} \; 1 - e^{A} \; n_s^2}$$

where Φ_s stands for the fluorescence quantum yield of standard (Rhodamine 6G; Φ_s = 95%[5]), $I(v)$ and $I_s(v)$ are the intensities of the sample and standard, respectively; A and A_s are the absorbances of the sample and standard, respectively, at the wavelength at which excitation of the compound has occurred; and n is the solvent refractive index (weighted arithmetic mean was calculated for $CHCl_3$-hexane and $CHCl_3$-CH_3OH mixtures with weights equal to vol% of components of the mixtures).

The results of the estimation of Φ_E are summarized below in Table S1.

Table S1. Summary of the estimated emission quantum yields (Φ_E).

$CHCl_3$-hexane mixtures			**$CHCl_3$- CH_3OH mixtures**		
Entry	Vol% (hexane)	Φ_E[a]	Entry	Vol% (CH_3OH)	Φ_E[a]
1	0	40%	1	0	42%
2	5		2	5	
3	10		3	10	
4	15	42%	4	15	
5	20		5	20	44%
6	30		6	30	45%
7	40	43%	7	40	47%
8	50		8	50	
9	60	45%	9	60	51%
10	70	64%	10	70	67%
11	80	77%	11	80	82%
12	90	86%	12	90	90%
13	95	89%	13	95	92%

[a] estimated by the relative method.

S5. DLS analysis

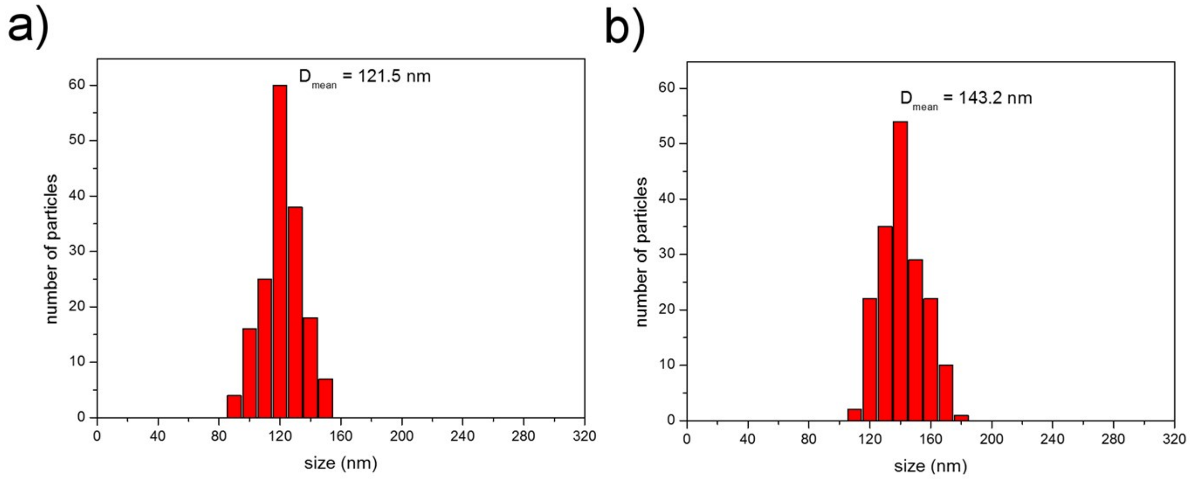

Figure S11. (**a**) DLS profile for the aggregates obtained from $CHCl_3$-CH_3OH mixture with 95 vol% of poor solvent (hex); (**b**) DLS profile for the aggregates obtained from $CHCl_3$-CH_3OH mixture with 95 vol% of poor solvent (CH_3OH).

S6. Job's plot analysis on the interactions between 5 and Cs$^+$

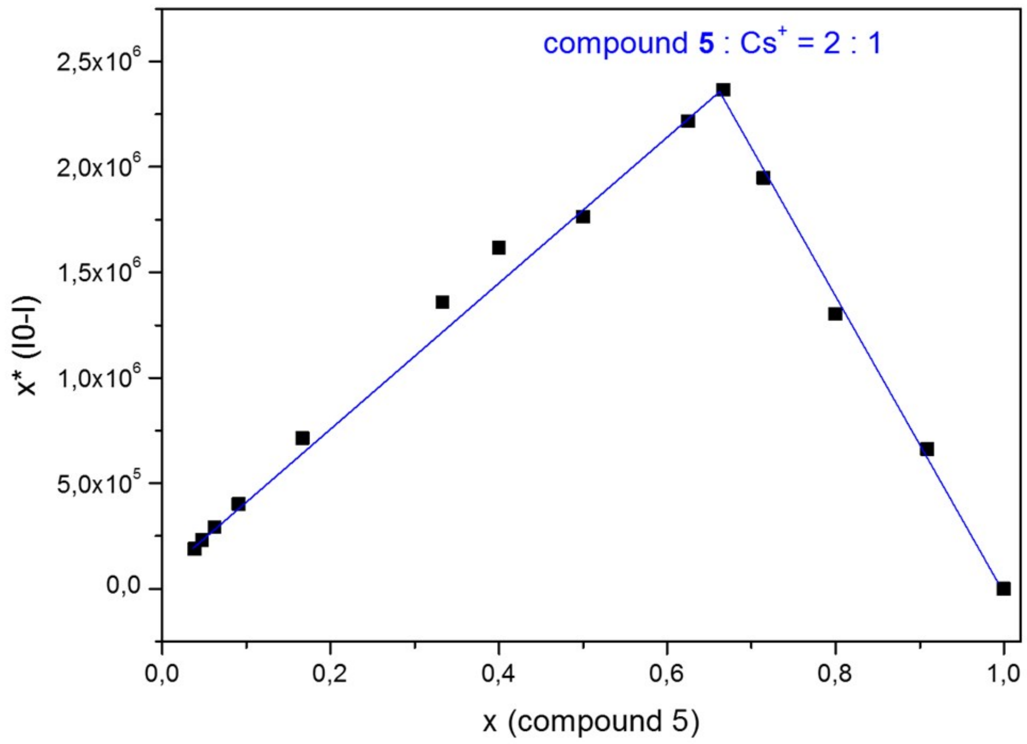

Figure S12. Job's plot regarding the studied interactions between **5** and Cs$^+$.

S7. Selectivity studies on the interactions between 5 and Cs^+

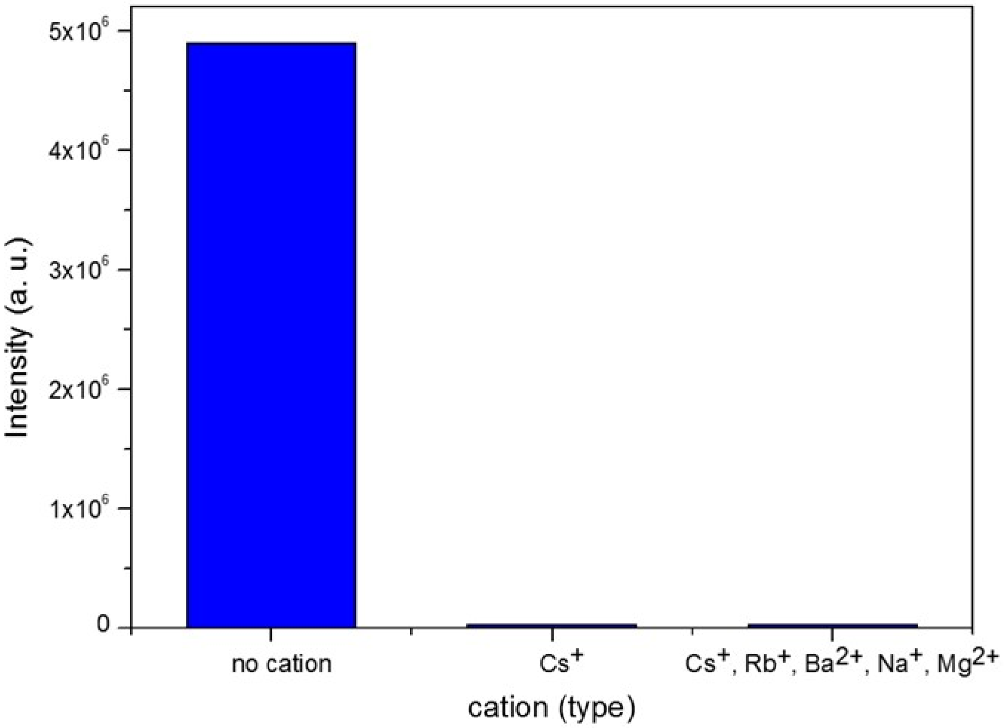

Figure S13. Comparison between emission intensity (λ_{em} = 548 nm) changes of aggregated **5** upon the addition of Cs^+ (25 equiv) and Cs^+ (25 equiv) in the presence of other cations (Rb^+, Ba^{2+}, Na^+, Mg^{2+}).

S8. Reversibility studies

To perform the reversibility studies, the following procedure was applied:

1. The sample after the treatment of aggregated **5** ($CHCl_3$-CH_3OH mixture with 95 vol% of poor solvent) with 2.0 equiv of Cs^+ was centrifuged (10000 rpm, 10 min). The supernatant was precisely removed.
2. The obtained solid was suspended in 2 mL of $CHCl_3$-CH_3OH (95 vol% of MeOH). The sample was intensively shaken for 1 hour (450 rpm) and centrifuged (10000 rpm, 10 min). The supernatant was precisely removed.
3. Step 3 was repeated three more times.
4. The obtained solid was subjected to the emission spectra measurement (λ_{ex} = 548 nm) in the presence or absence of 2.0 equiv of Cs^+. The results are presented in **Fig. S14**.

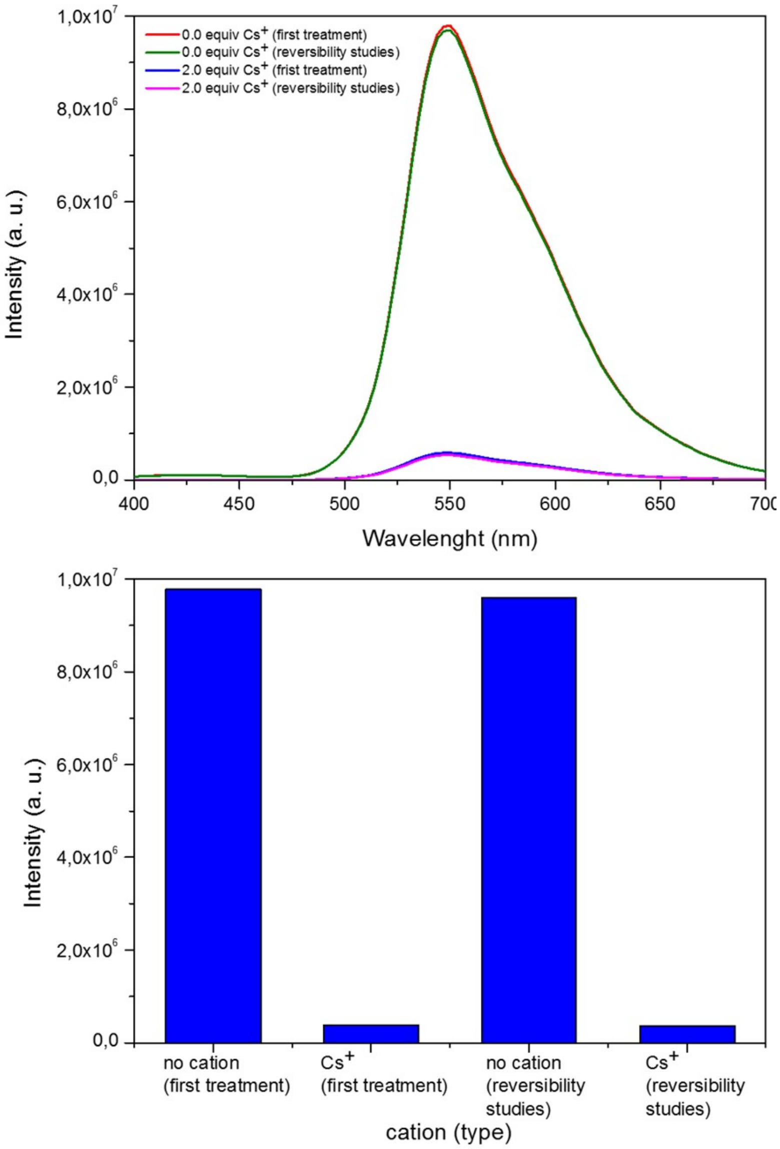

Figure S14. Results of the reversibility studies with aggregated **5**: **(top)** emission spectra (95 vol% CH_3OH in $CHCl_3$; $2{\cdot}10^{-5}$ M; λ_{ex} = 360 nm); **(bottom)** emission intensity (λ_{em} = 548 nm) changes aggregated **5** upon the addition of Cs^+ (2.0 equiv).

S9. Calculation of binding constant

The association constant was determined with Benesi-Hildebrand equation:

$$\frac{1}{I - I_0} = \frac{1}{a} + \frac{1}{a \cdot K_a \cdot C(Cs^+)}$$

where I_0 and I are the fluorescence intensities of **5** in the absence and presence of Cs^+, respectively, and a is a constant, K_a is the association constant, $C(Cs^+)$ is the concentration of Cs^+ in solution. The association constant was determined as a ratio of intercept-to-slope of $1/(I - I_0)$ vs. $1/C(Cs^+)$ linear plot (Fig. S15). R^2 value for this linear plot was 0.9922.

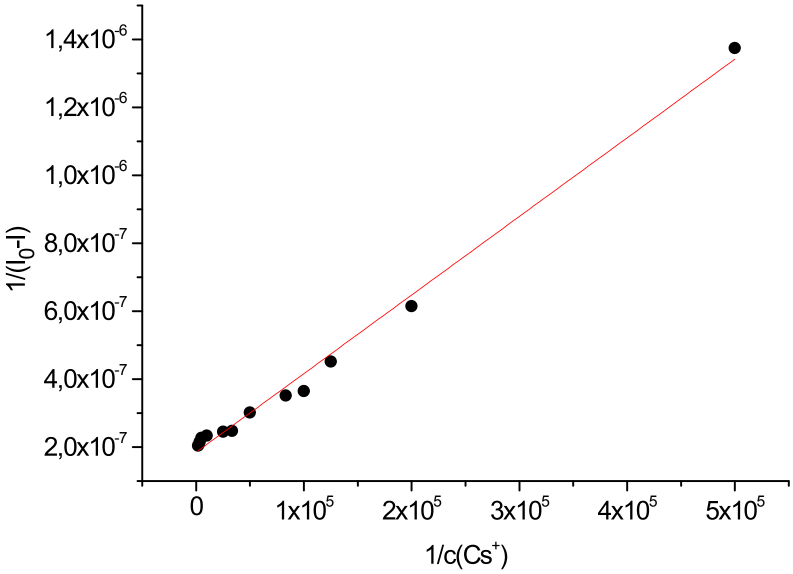

Figure S15. Benesi–Hildebrand plot from emission spectra data of aggregated **5** in the presence of Cs^+.

S10. References

1. M. Jung, J. Lee, H. Jung, S. Kang, A. Wakamiya, J. Park. *Dyes Pigm.*, **2018**, *158*, 42-49.
2. H. Sakurai, T. Daiko, T. Hirao. *Science*, **2003**, *301*, 1878.
3. J. Yang, Q. Guo, J. Wang, Z. Ren, J. Chen, Q. Peng, D. Ma, Z. Li. *Adv. Opt. Mater.,* **2018**, *6*, article no.1800342.
4. For the details of this methodology, see: M. Urban, K. Durka, P. Jankowski, J. Serwatowski, S. Lulinski, *J. Org. Chem.*, **2017**, *82*, 8234.
5. According to IUPAC data, see: A. M. Brouwer, *Pure Appl. Chem.*, **2011**, *83*, 2213.