SUPPORTING INFORMATION

Stable Ultrabright Nanoprobes for Two-Photon Microscopy Based on Octupolar Merocyanine-loaded Nanovesicles

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Table of contents

Table S1. Description of dye-loaded QS.

Table S2. Quantities used for the preparation of dye-loaded QS using the DELOS-SUSP process.

Table S3. Physicochemical and spectroscopical characterization of quatsomes loaded with dyes 4, 5, 6, and 7

Table S4. Exponential components analysis obtained from reconvolution fits of bi-exponential emission decays.

Table S5. Geometric parameters of dye-loaded QS.

Table S6. Calculation of the number of dye molecules per QS.

Table S7. Brightness one-photon and two-photon per particle calculations.

Table S8. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the simplified single-arm chromophore (transoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

Table S9. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the simplified single-arm chromophore (cisoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

Table S10. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the three-arm chromophore (transoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

Table S11. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the three-arm chromophore (cisoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

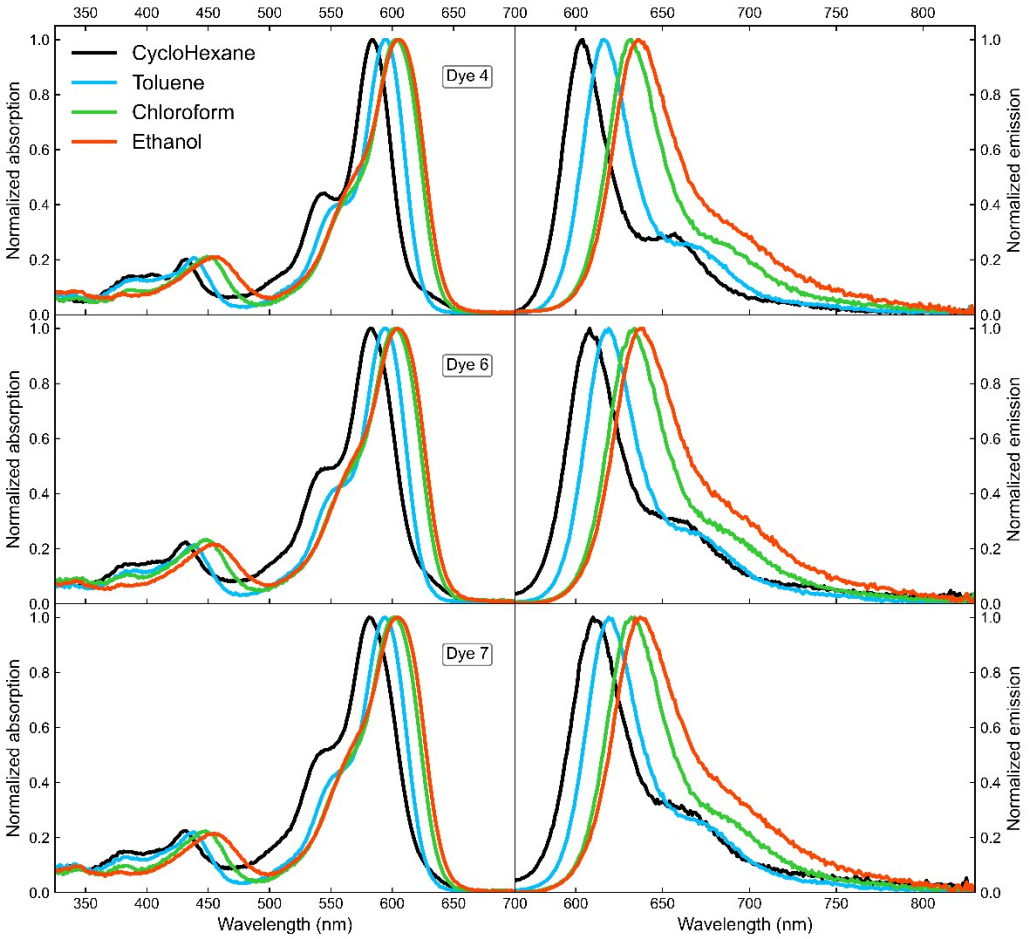

Figure S1. **Normalized absorbance (left panel) and emission spectra (right panel, λ_{exc} = 560 nm) of dyes 4, 6, and 7 in solvents of different polarity**.

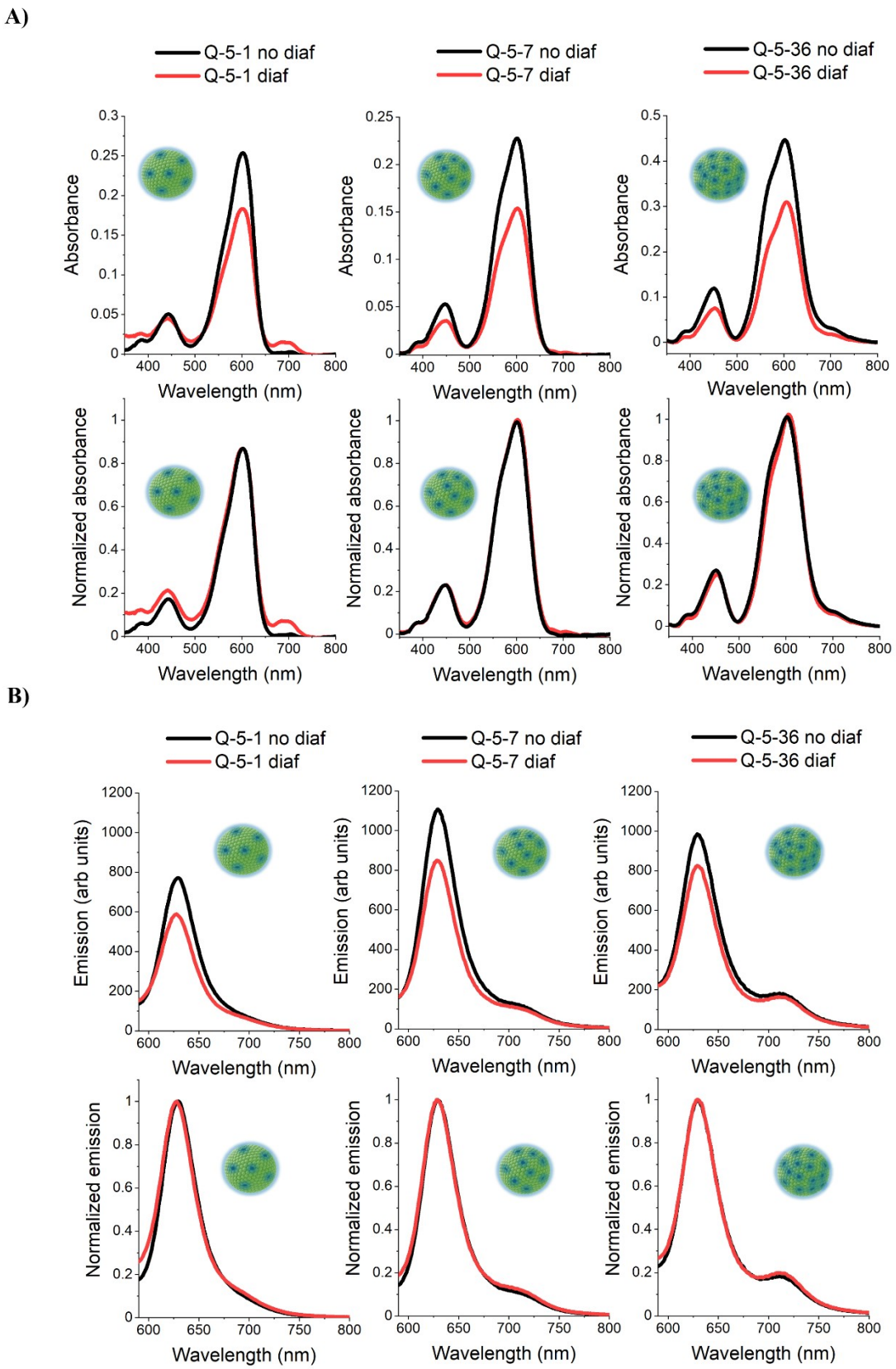

Figure S2. **Absorbance and emission spectra of dye 5 loaded quatsome dispersions, pre- and post-diafiltration**. Absorbance and emission intensities showed a certain decrease upon diafiltration (of up to ~ 33% and ~23%, respectively) while normalized spectra remained mainly unchanged.

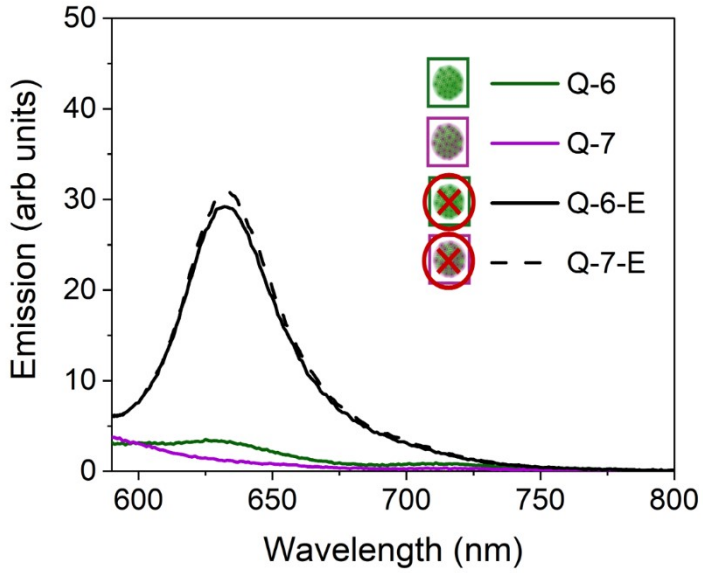

Figure S3. Emission spectra of quatsomes loaded with dyes 6 and 7 after dissolution in EtOH. The restoration of emission spectra upon vesicle disruption (Q-6 and Q-7) and dissolution in EtOH confirms that the dyes had not been properly stabilized within the nanovesicles.

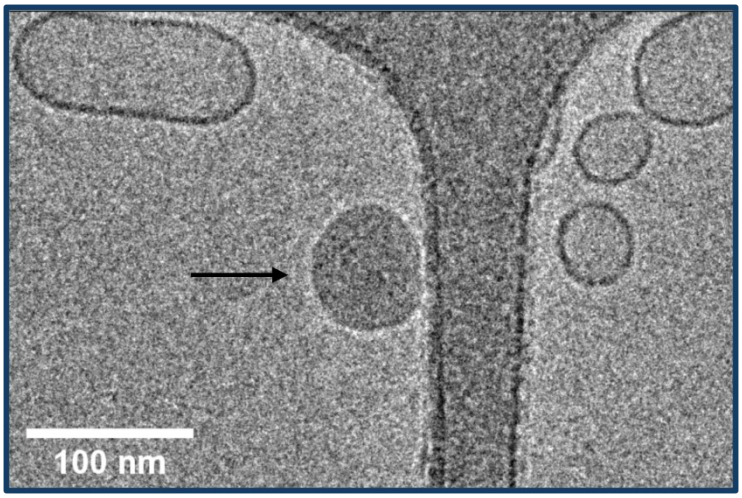

Figure S4. Cryo-TEM image of a non-vesicular structure observed for formulation Q-5-36 (black arrow).

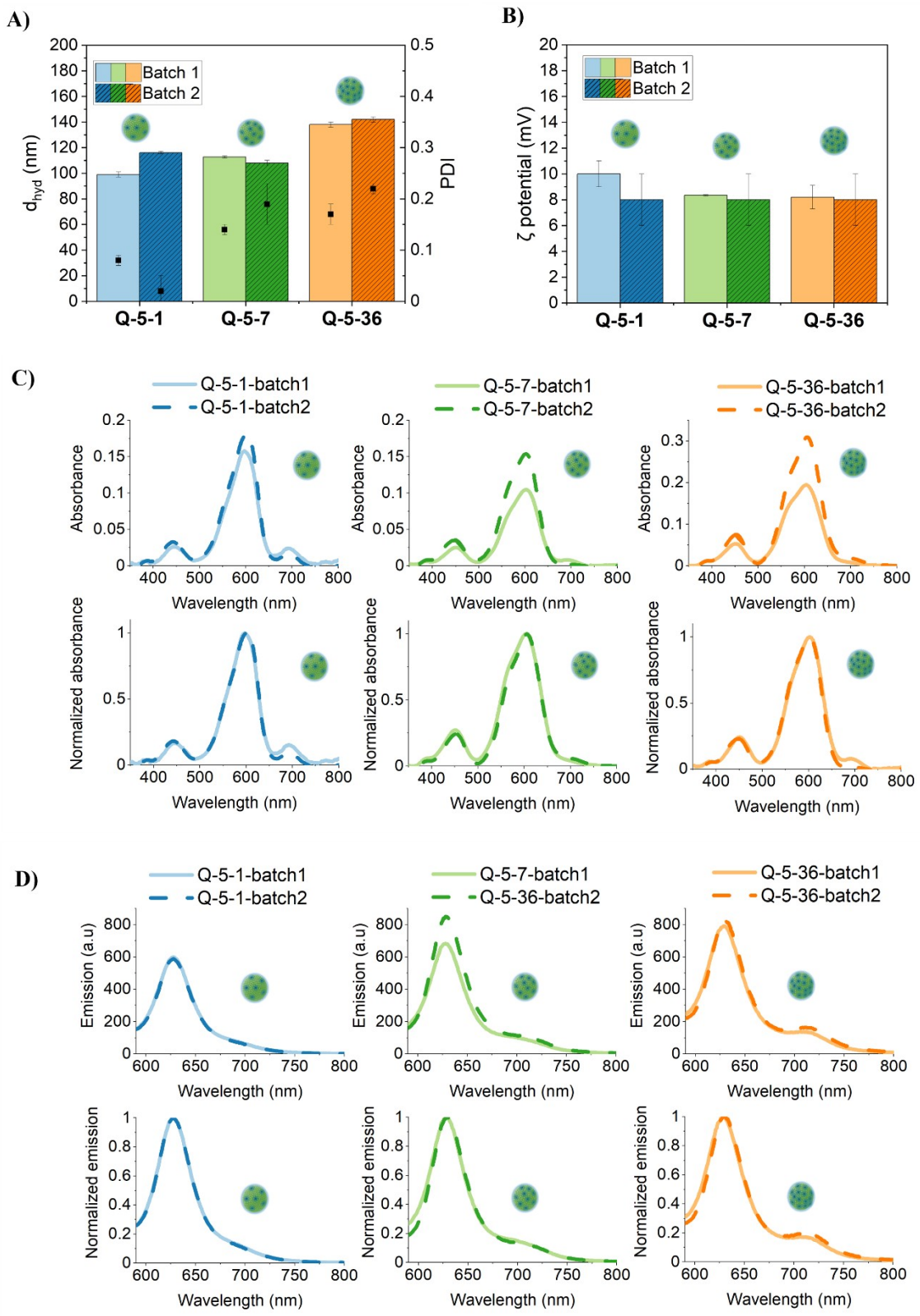

Figure S5. **Batch-to-batch reproducibility. (A)** Size and dispersity (Đ), **(B)** ζ-potential, **(C)** absorbance, and **(D)** emission spectra of two replica (N=2) of Q-5 containing different dye loadings (Q-5-1, Q-5-7, and Q-5-36). The batches are highly reproducible among themselves, as they have very similar sizes, Đ and zeta potentials, and the normalised absorbance and emission spectra are practically identical. However, in the case of batch 1, for intermediate and high loadings, the absorbance spectra are slightly higher in intensity. This occurs because there are slight differences in the % of dye loading obtained.

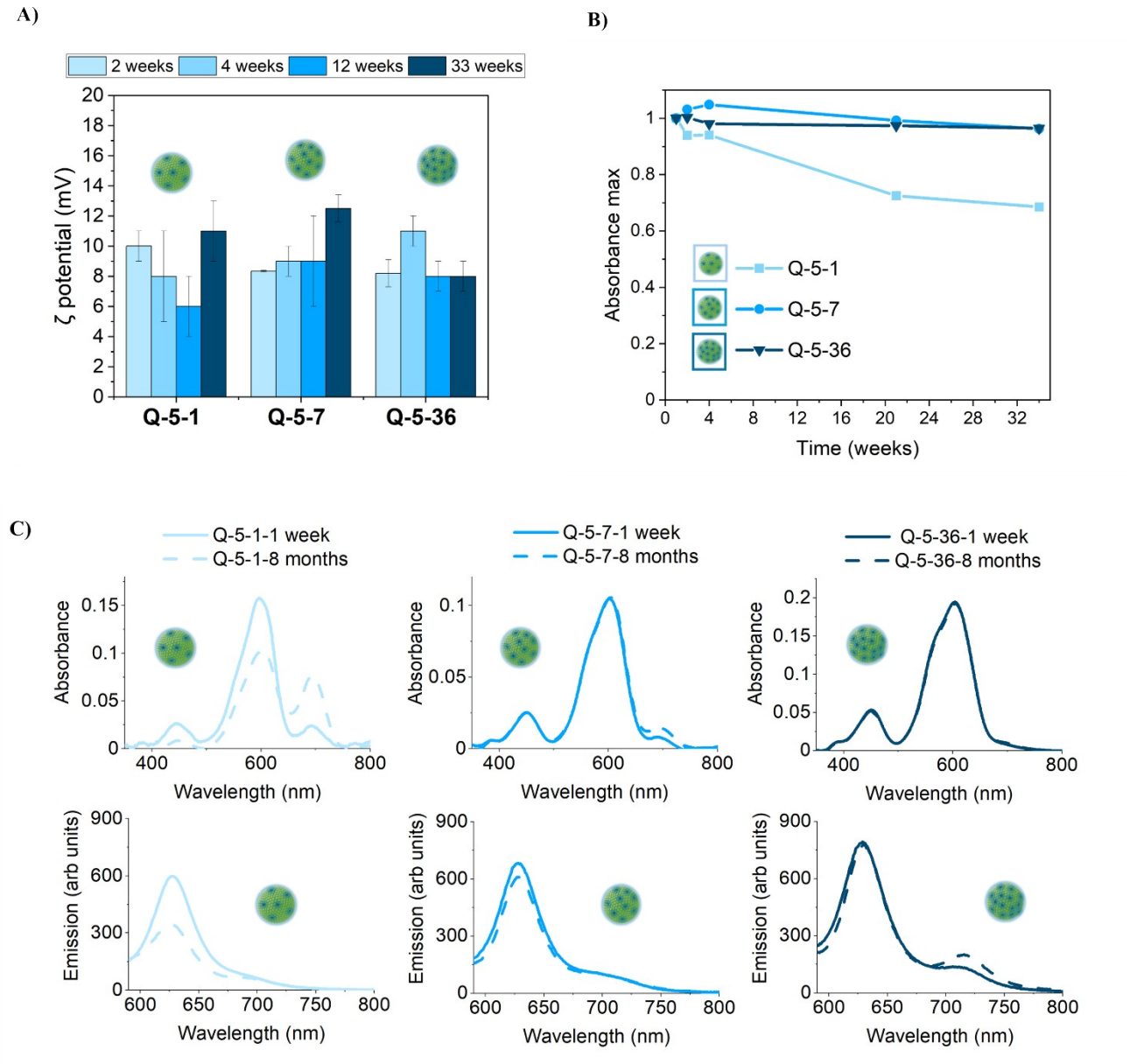

Figure S6. **Colloidal and optical stability of dye-loaded QS over the time course of 8 months**. **(A)** Evolution of the ζ-potential. **(B)** Maximum absorbance over time. **(C)** Absorbance and emission spectra after 8 months, compared with fresh samples.

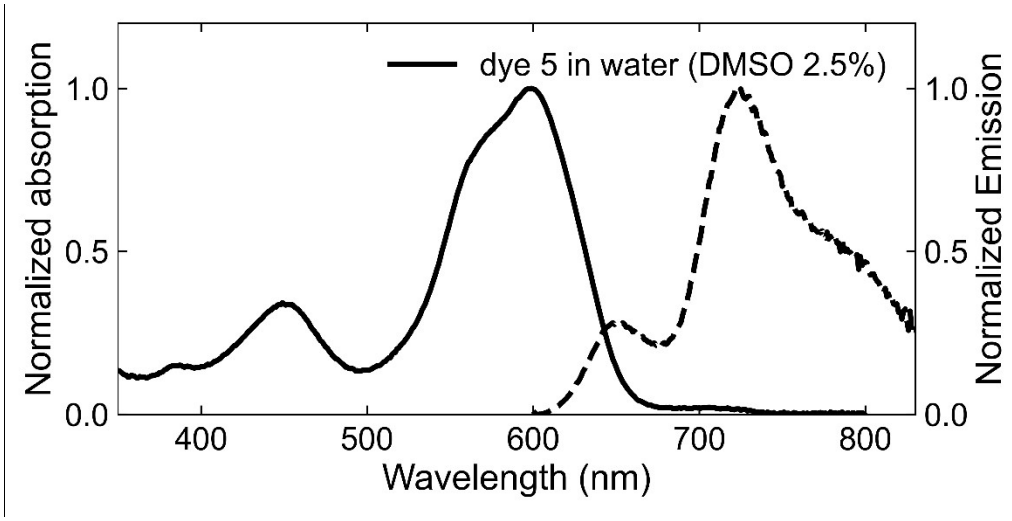

Figure S7. **Normalized absorption and emission spectra of dye 5 dispersed in water with a 2.5% of DMSO** (v/v). The estimated fluorescence quantum yield of the dye in these conditions resulted lower than 1%.

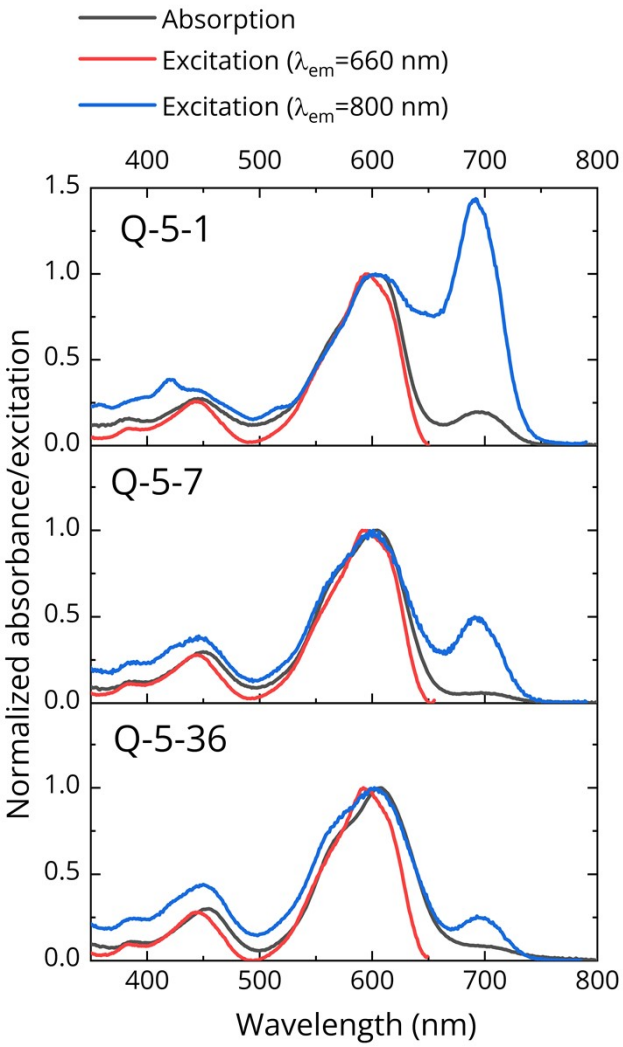

Figure S8. **Excitation spectra of Q-5 dispersions with different dye loadings**, recorded at λ_{em} = 660 nm (red line) and at 800 nm (blue line), co-plotted with absorbance spectra (black line).

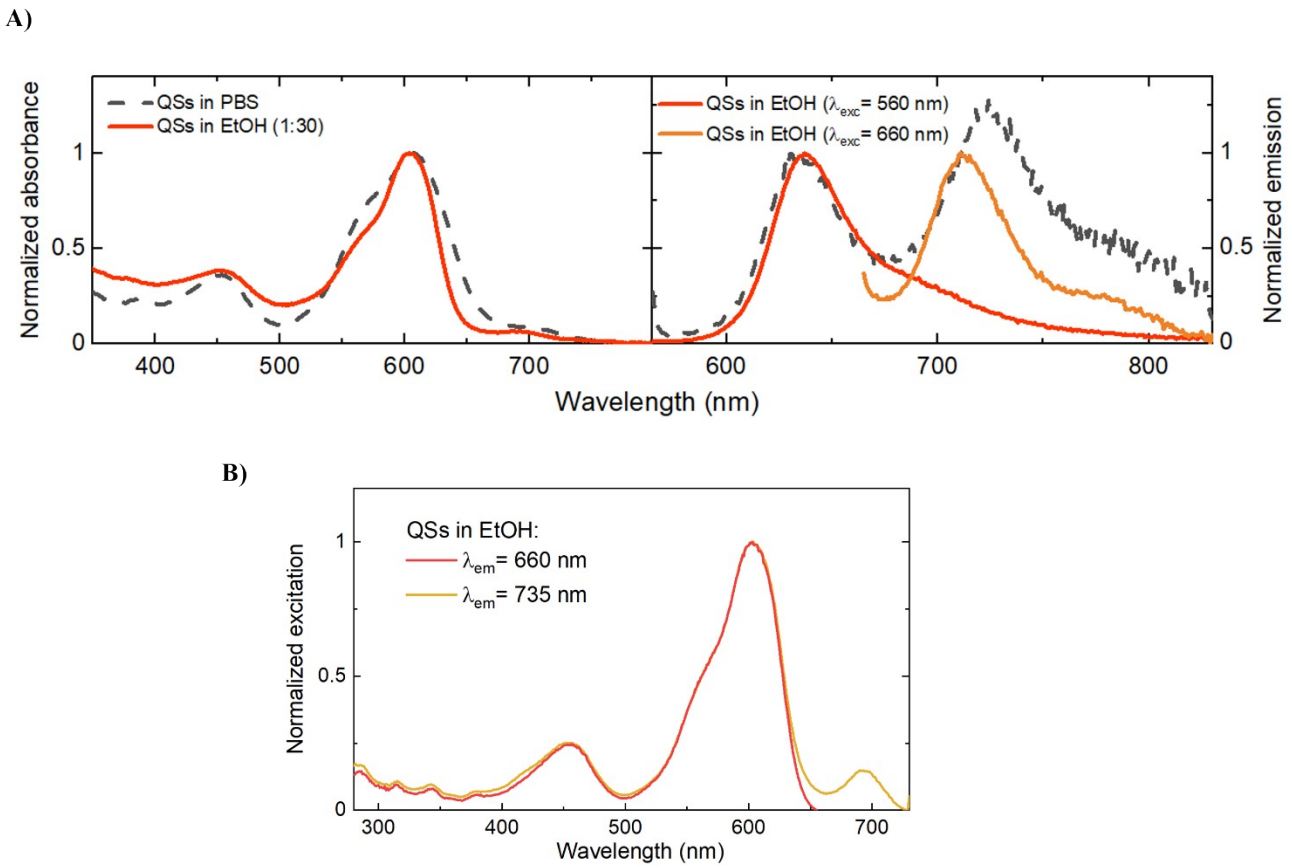

Figure S9. **Absorbance, emission, and excitation spectra of Q-5-36 after the dissolution of membrane components in EtOH** (1:30) (solid red and orange lines), compared with spectra obtained for the Q-5-36 nanoparticle dispersion in PBS (dashed black lines).

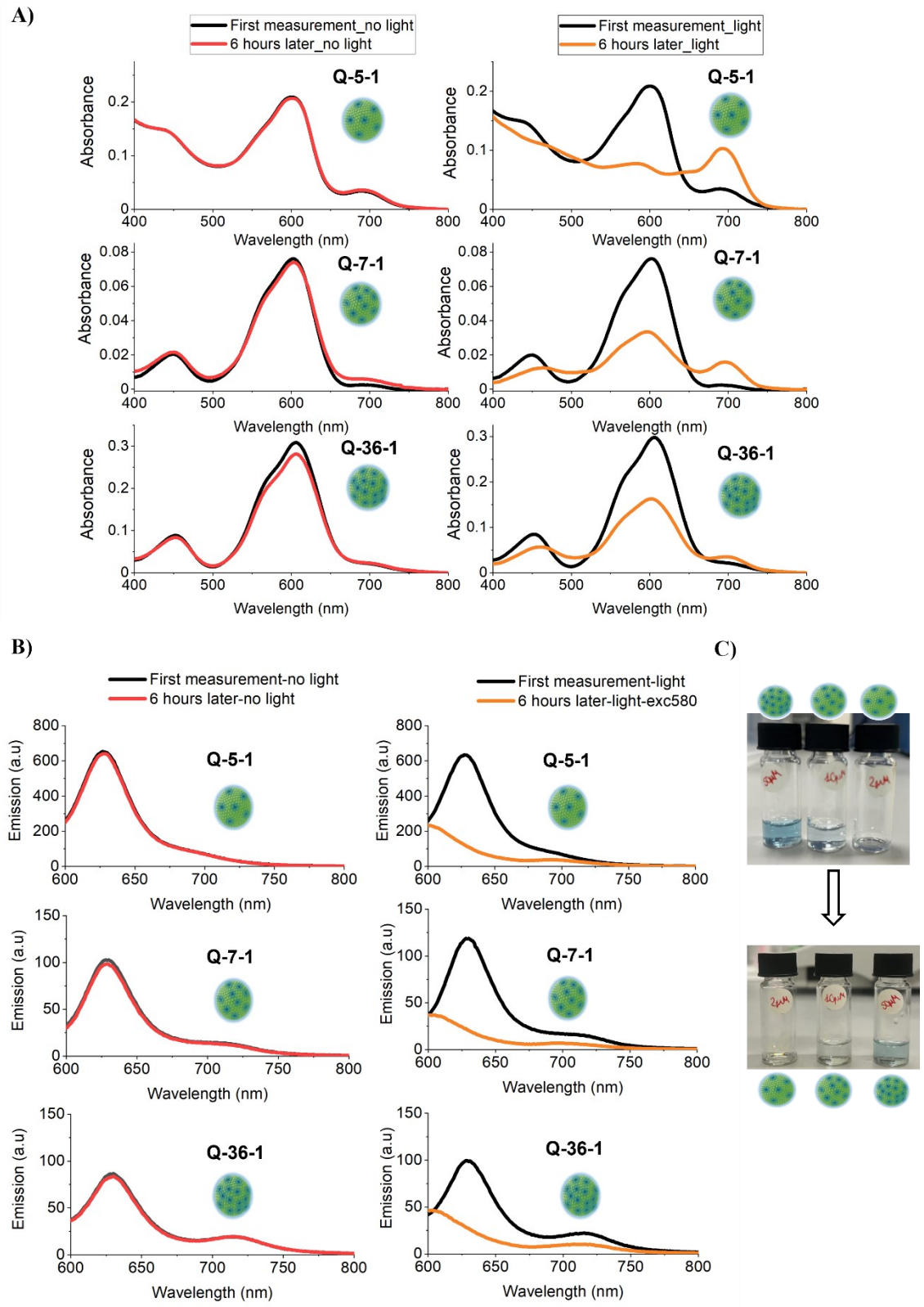

Figure S10. **Impact of exposure to ambient light on absorbance and emission spectra**. Samples that were protected from light (solid red lines) did not show any significant changes in absorbance **(A)** and emission spectra **(B)**. On the contrary, samples exposed to ambient light during six hours (solid orange lines) showed a clear decrease of the main absorbance peak at ~ 600 nm and a strong increase of the secondary peak at ~ 700 nm, indicating light-induced degradation. Emission spectra showed a strong decrease in intensity after light exposure. **(C)** Loss in coloration observed macroscopically after 6 hours of exposure to light.

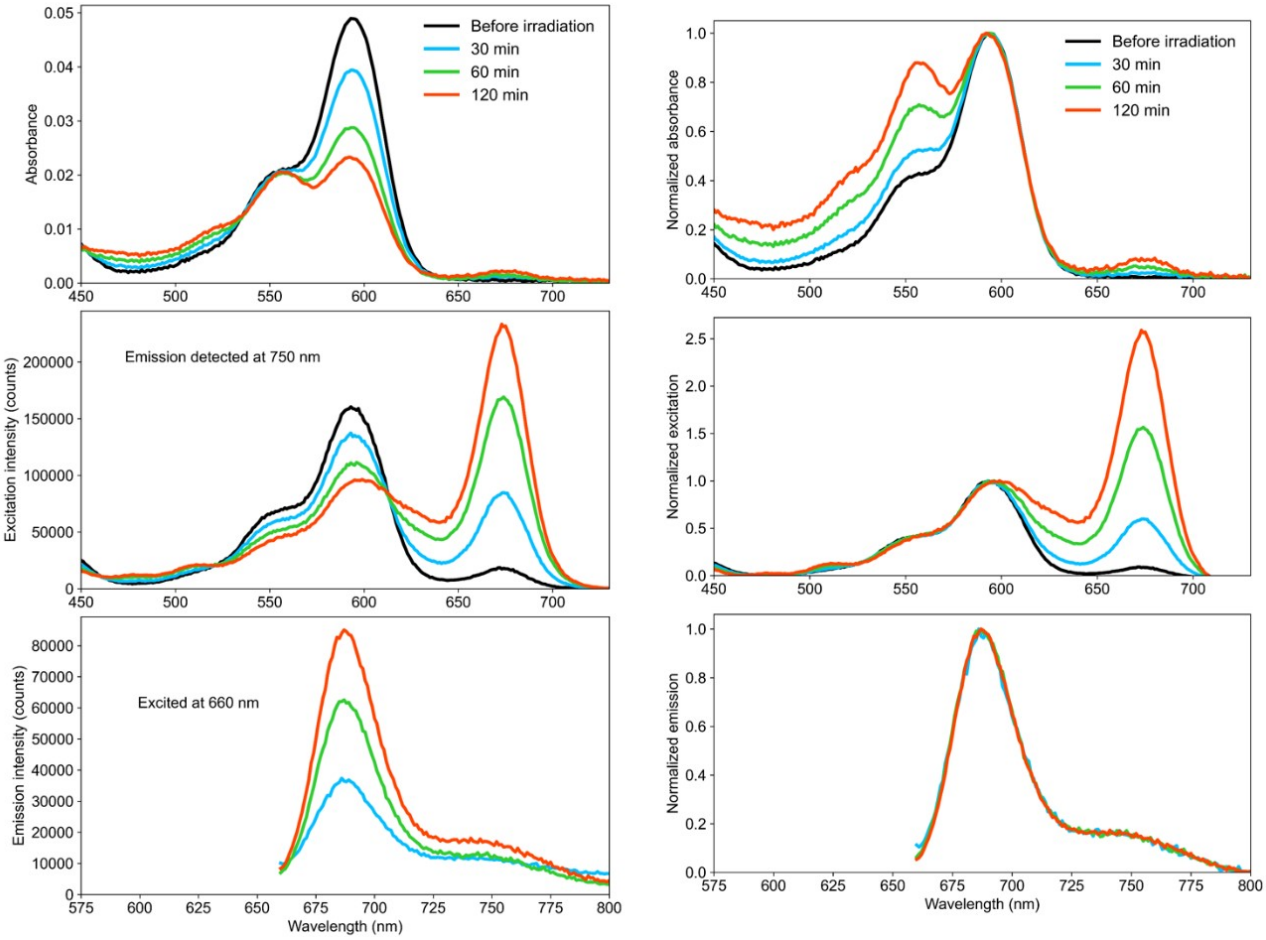

Figure S11. Impact of exposure to 630 nm light on absorbance, excitation and emission spectra of dye 5. Left: Absorbance (top), excitation (middle) and emission (bottom) spectra of dye **5** collected after different time exposure to light at 630 nm. Right: same as left, but normalized spectra. By increasing the time exposure, the maximum of the absorbance spectrum decreases, and a weak band at 670 nm gradually acquires intensity. In excitation spectra, collected detecting emitted light at 750 nm, the band at 670 nm becomes much more intense as time of light exposure increases. Exciting the sample at 660 nm, the emission band observed at 680 nm acquires intensity as the time of light exposure increases.

DFT and TD-DFT calculations on transoid and cisoid isomers

For the single-arm model, the $S_0 \rightarrow S_1$ transition was found to be predominantly HOMO → LUMO in character (panels **c** and **f**) and 0.08 eV lower in energy for the cisoid isomer relative to the transoid one, consistent with a bathochromic shift (panels **b** and **e**). This trend persists in the three-arm molecule (panels **a** and **d**, in **Figure S12**), where TD-DFT calculations reveal that the two lowest-energy excited states, mainly HOMO → LUMO and HOMO-1 → LUMO in character (see panels **c** and **f**), are red-shifted in the cisoid conformation (see panels **b** and **e**). Similarly, the two higher-lying dark states (S_3 and S_4) also decrease slightly in energy upon twisting to the cisoid geometry. The cis-trans isomerization can then potentially explain the absorption band experimentally observed at 700nm in QS loaded with dye **5**.

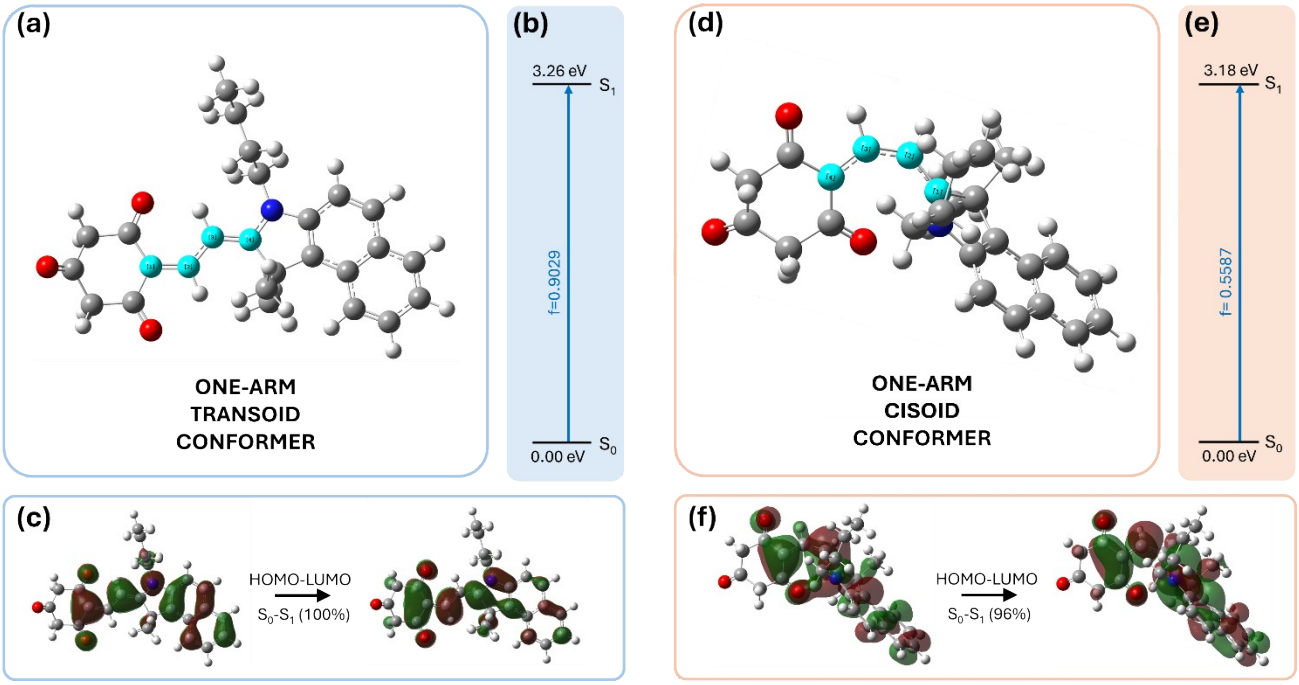

Figure S12 Simplified structure containing a single chromophoric arm. (a) Molecular structure of the transoid isomer; **(b)** simplified Jablonski diagram of the transoid isomer with the oscillator strength *f* relevant to the $S_0 \rightarrow S_1$ transition; **(c)** the most important Kohn-Sham molecular orbitals involved in the $S_0 \rightarrow S_1$ transition. Panels **(d-f)** report the corresponding results for the cisoid isomer. In **(a)** and **(d)**, the atoms defining the dihedral rotation used to generate the two isomers are highlighted in blue. All calculations were performed at the CAM-B3LYP/6-31G(d,p) level.

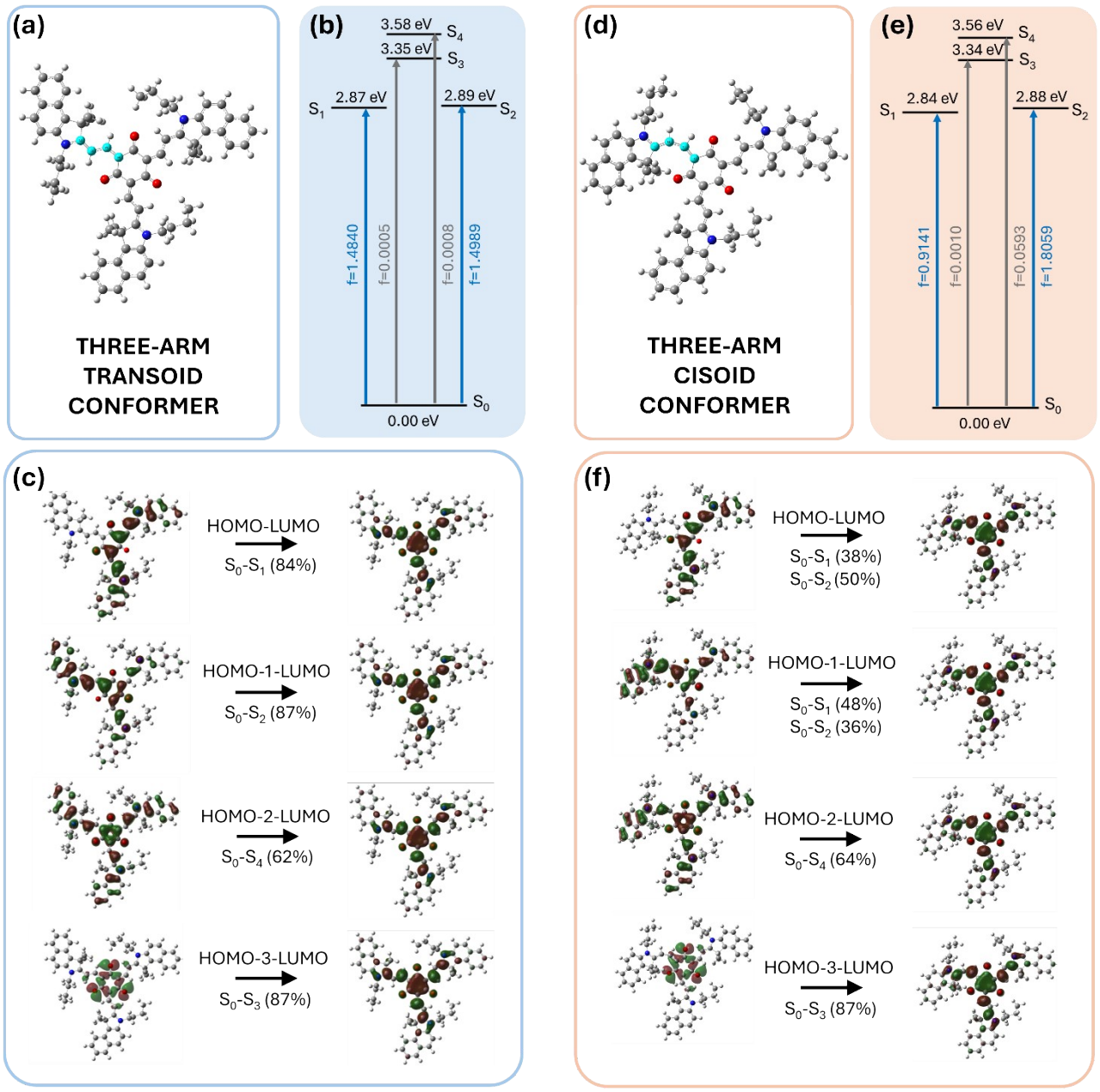

Figure S13. Results for the transoid and cisoid conformers of the three-arm molecule. **(a)** Molecular structure of the transoid isomer; **(b)** simplified Jablonski diagram of the transoid isomer with oscillator strengths *f* relevant to the first four electronic transitions; **(c)** key Kohn-Sham molecular orbitals involved in the first four transitions. Panels **(d-f)** show the corresponding results for the cisoid isomer. In **(a)** and **(d)**, the atoms defining the dihedral rotation used to generate the two isomers are highlighted in blue. All calculations were performed at the CAM-B3LYP/6-31G(d,p) level.

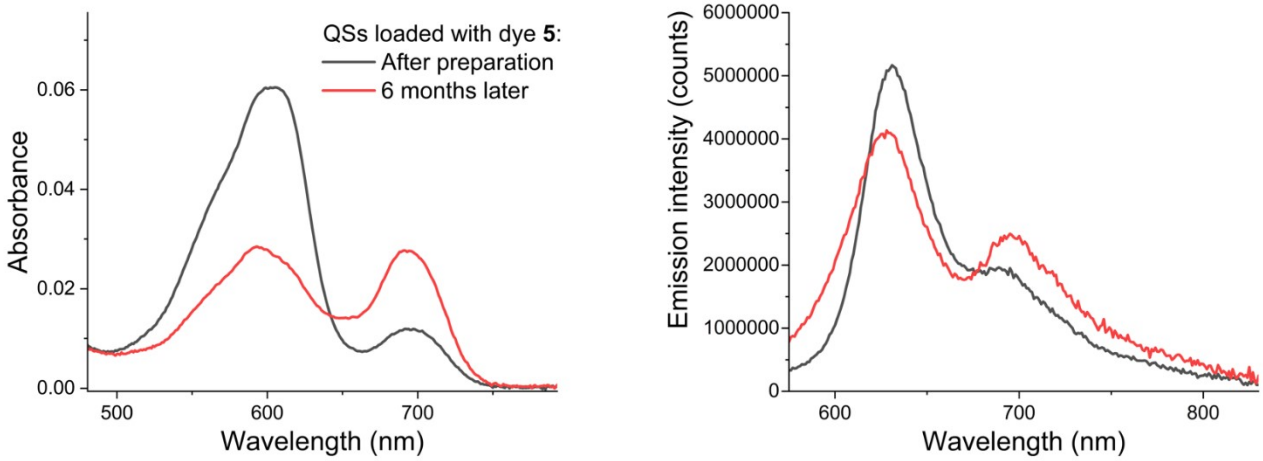

Figure S14. **Absorption (left) and emission (right, acquired exciting the sample at 560 nm) spectra of a QSs suspension (QS-5-36) after preparation and after 6 months**. The emission profiles have been divided by the absorbance at the excitation wavelength to compare the emission quantum yield of the two suspensions.

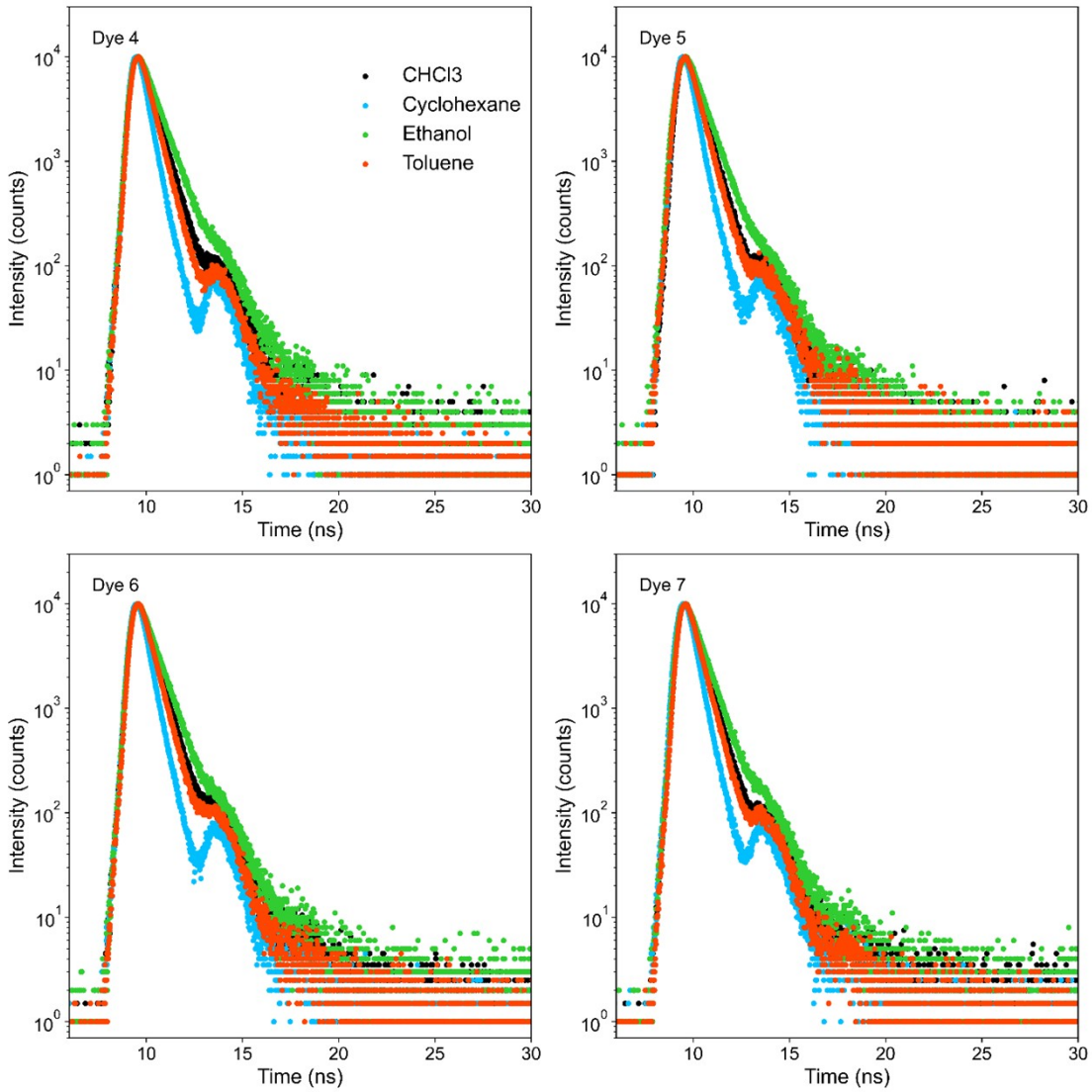

Figure S15. Fluorescence lifetimes decays of dyes 4, 5, 6, and 7 in solvents of different polarity. All the data have been obtained by exciting the sample with a ps pulsed laser (405 nm) and collecting the sample emission at in correspondence of the emission peak.

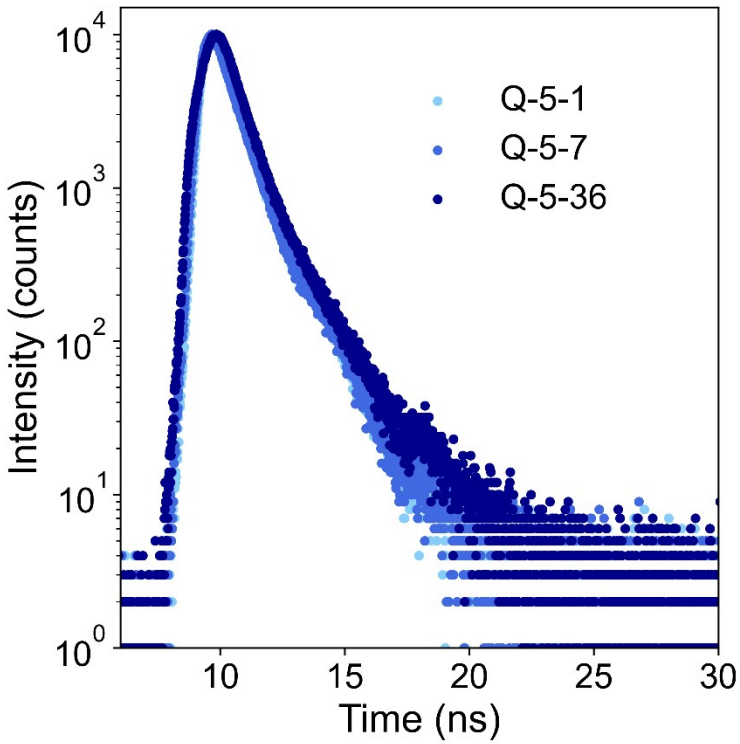

Figure S16. **Fluorescence lifetime decays of the three quatsome dispersions with different dye 5 loadings**, recorded at λ_{em} = 660.

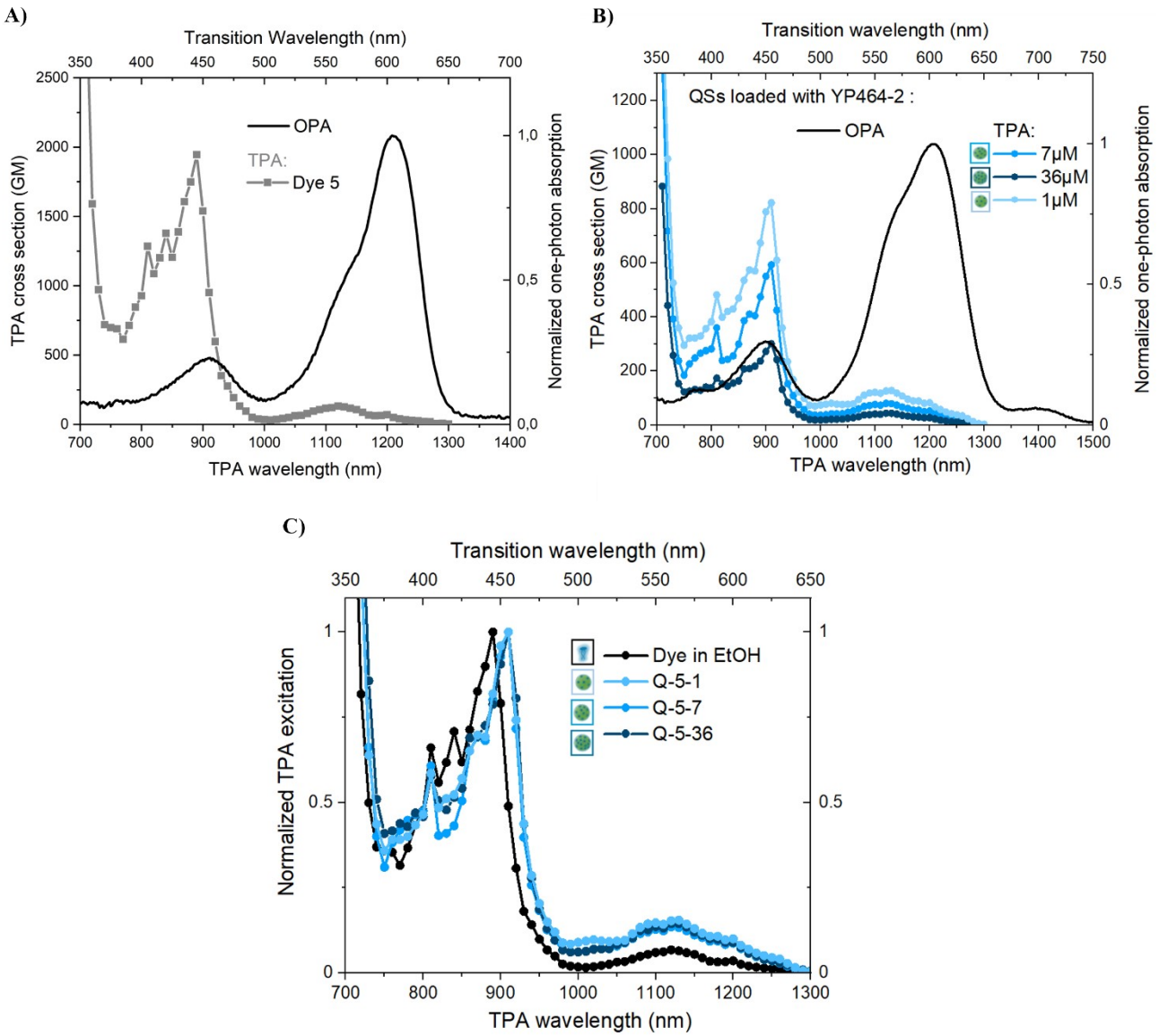

Figure S17. The two-photon absorption (TPA) cross-section of dye 5-loaded quatsomes. A) TPA cross section of dye **5** free in EtOH, compared to its one-photon absorption (OPA) emission spectra, **B)** TPA cross section of Q-**5** with different loadings compared to their OPA emission spectra, **C)** Normalized TPA spectra of dye **5** and dye **5**-loaded QS.

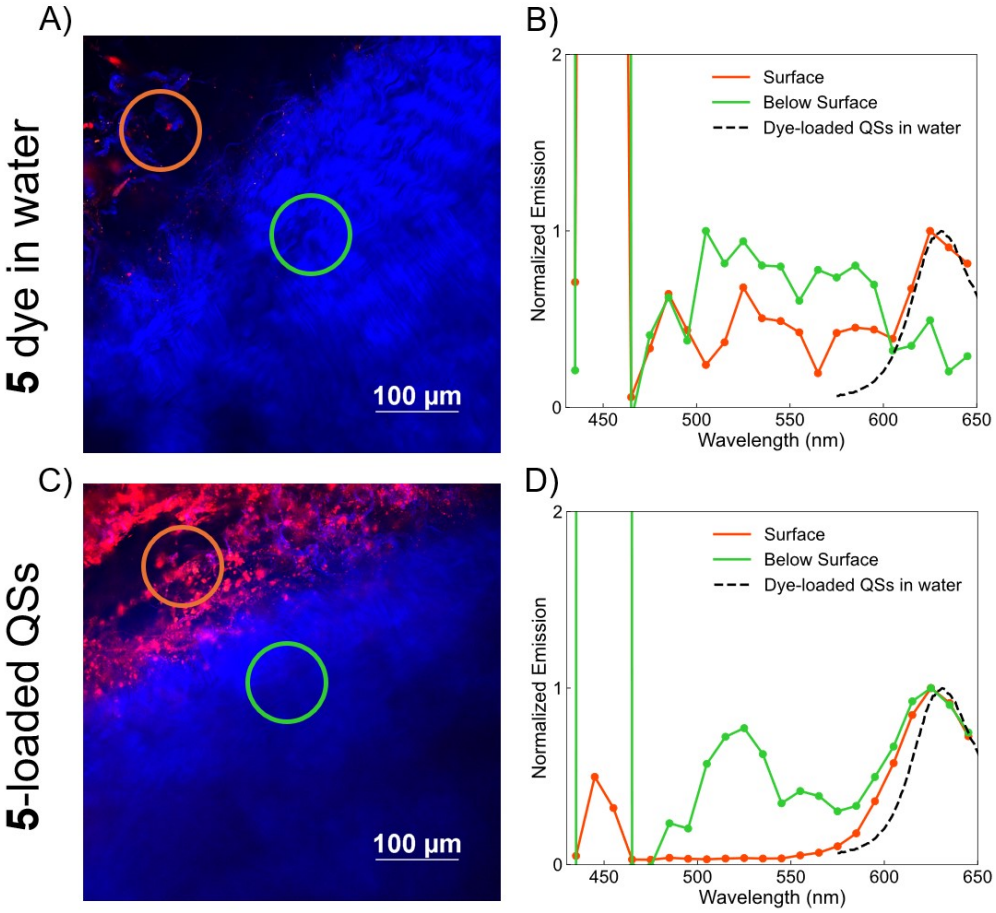

Figure S18. **Two-photon microscopy images of porcine scleral tissue treated with dye 5, either as a free solution in water with 2.5% DMSO (A) or loaded in QSs (C)**. Emission spectra collected from two regions of interest, one at the tissue surface (orange circle) and one at a deeper layer (green circle), are shown in panels (**B**) and (**D**) for the free **5** dye and the **5**-loaded QS-treated samples, respectively. The emission of **5**-loaded QSs acquired with a fluorimeter (black dashed line) is reported as a comparison. The images and emission spectra were acquired exciting the sample at 900 nm. The very intense peak observed at 450 nm corresponds to the SHG signal stemming from the collagen fibers of the tissue.

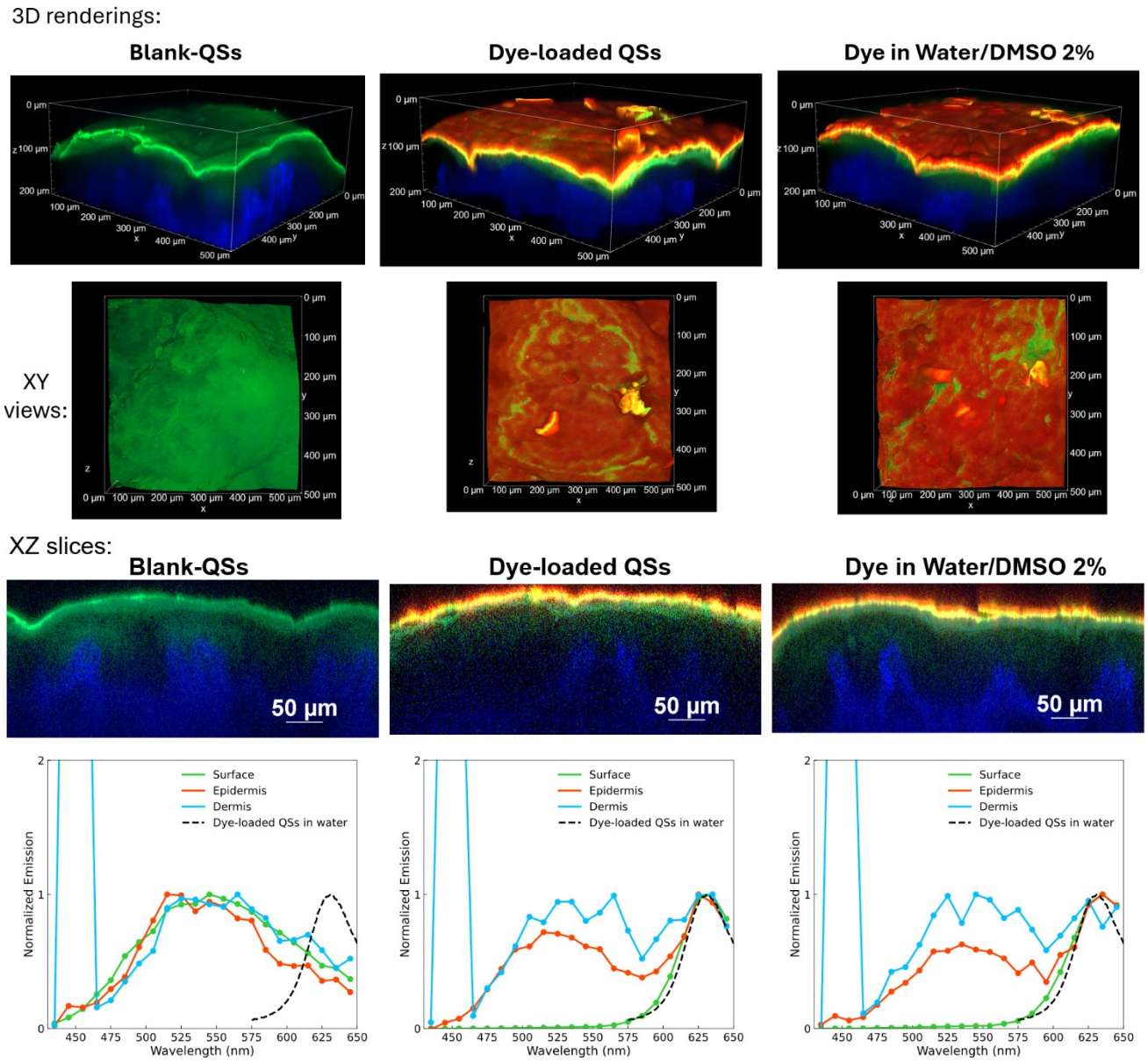

Figure S19. **Two-photon microscopy analysis of porcine skin tissues after 2-hour exposure to the blank QSs (left panels) and 5 dye, either loaded in QS (central panels) or as a free solution in water (with 2.5% DMSO, right panels)**. From top to bottom are reported the 3D rendering, XY views and XZ slices extracted from Z-stacks (for all samples: step size of 2 µm; total depth of 200 µm) and the emission spectra collected in correspondence of different tissue regions. All the images and emission spectra have been acquired with an excitation wavelength of 900 nm.

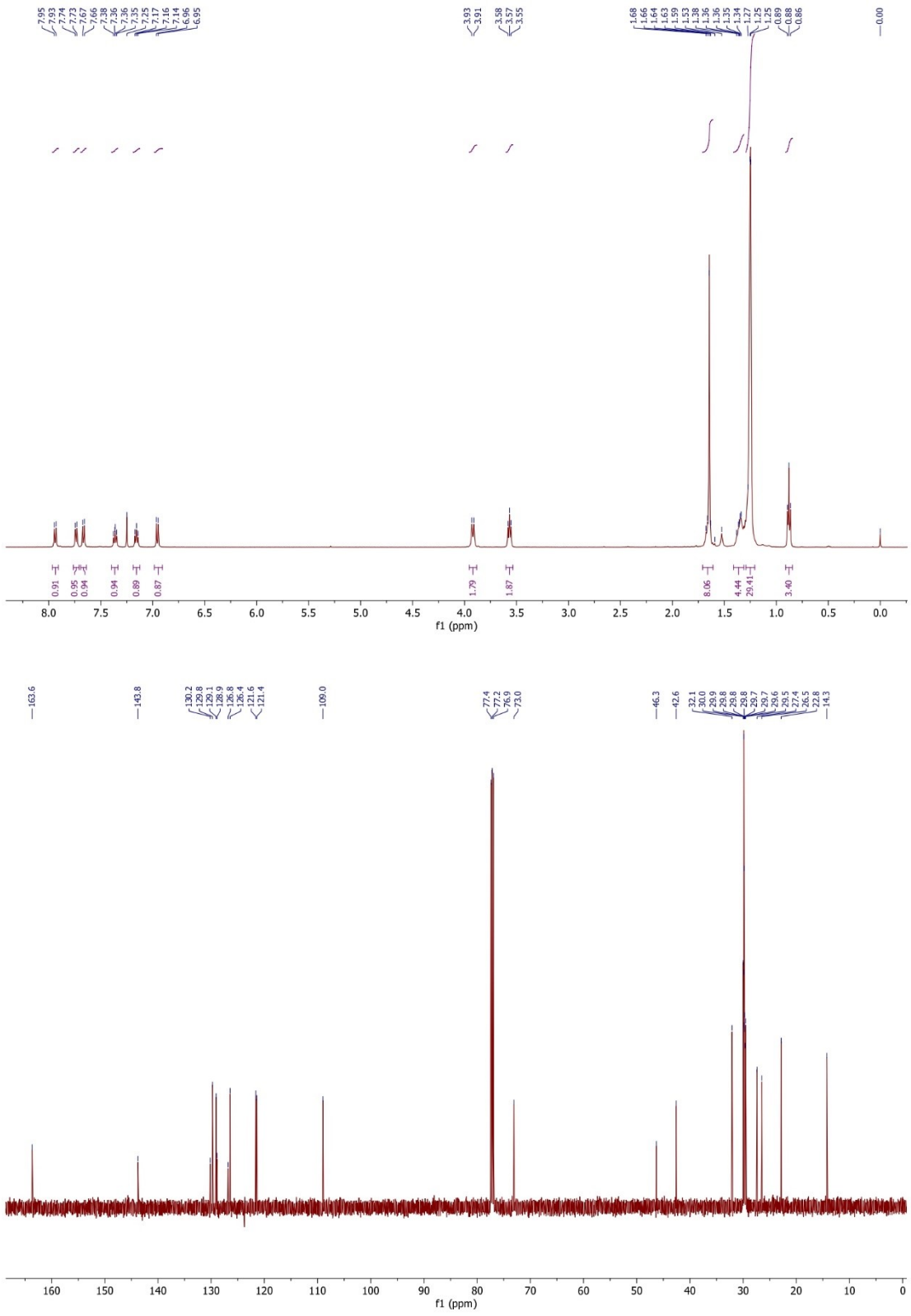

Figure S20. **^{1}H and ^{13}C NMR spectra for compound 2a in $CDCl_3$.**

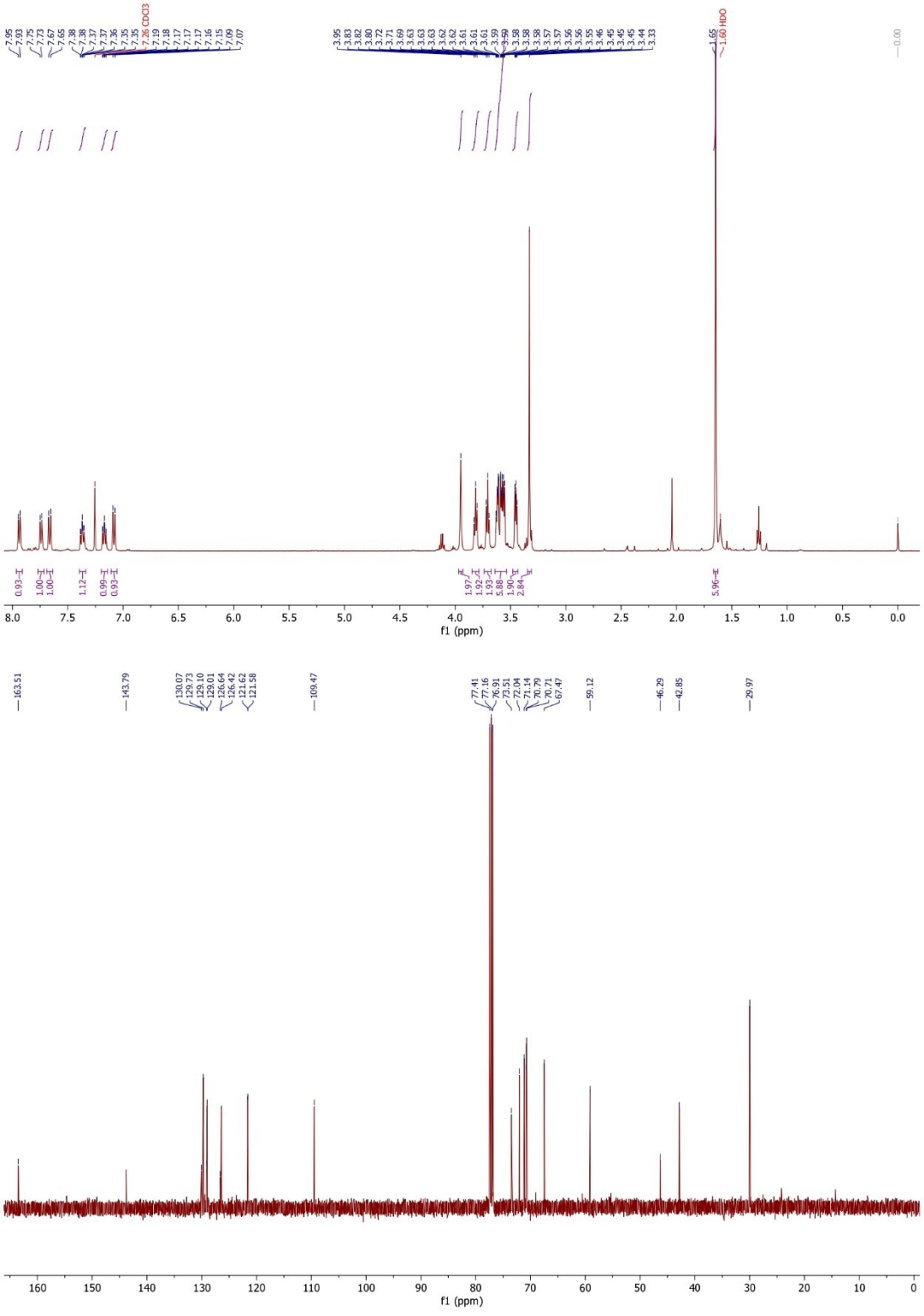

Figure S21. **^{1}H and ^{13}C NMR spectra for compound 2b in $CDCl_3$.**

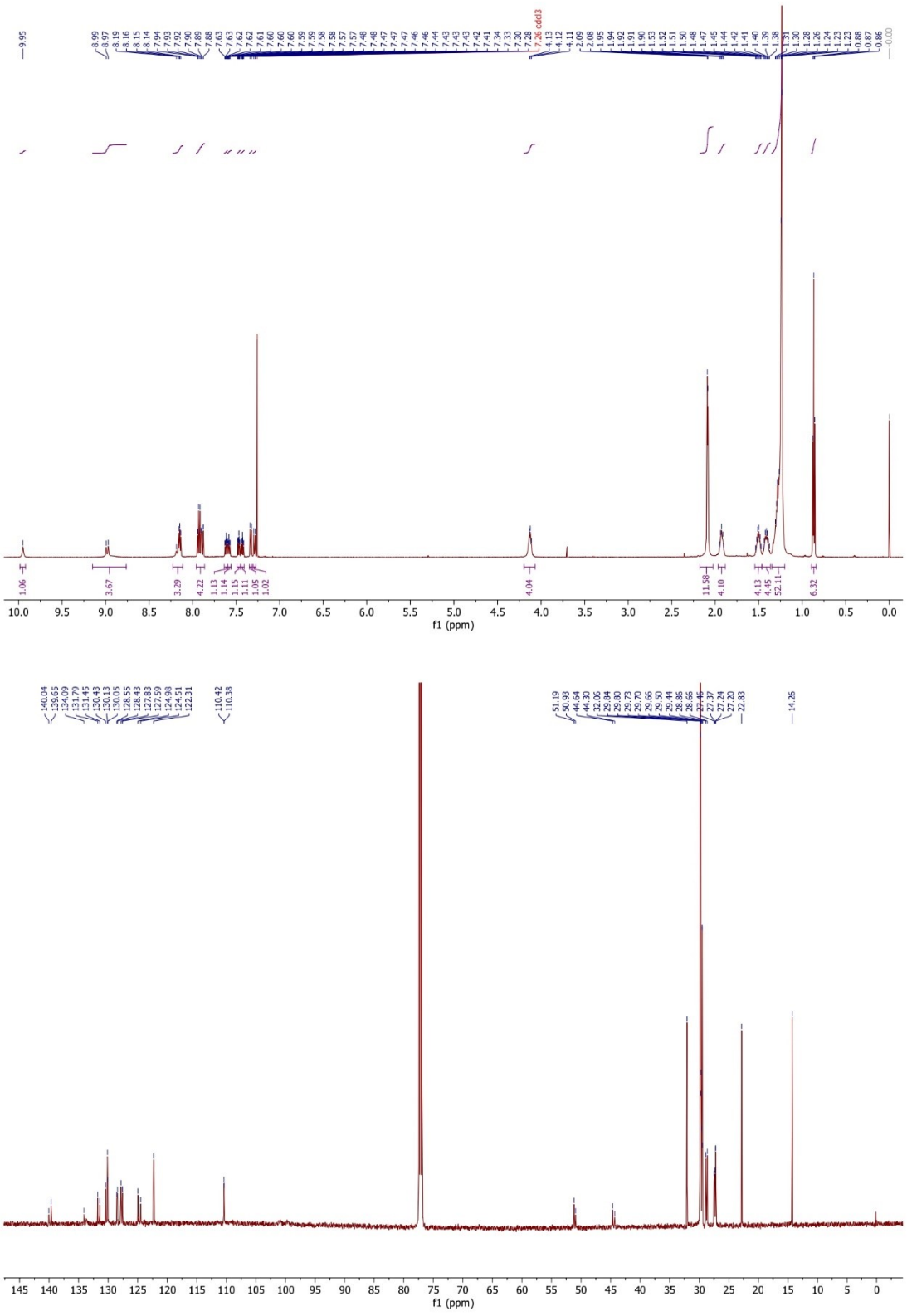

Figure S22. **^{1}H and ^{13}C NMR spectra for compound 3a in $CDCl_3$.**

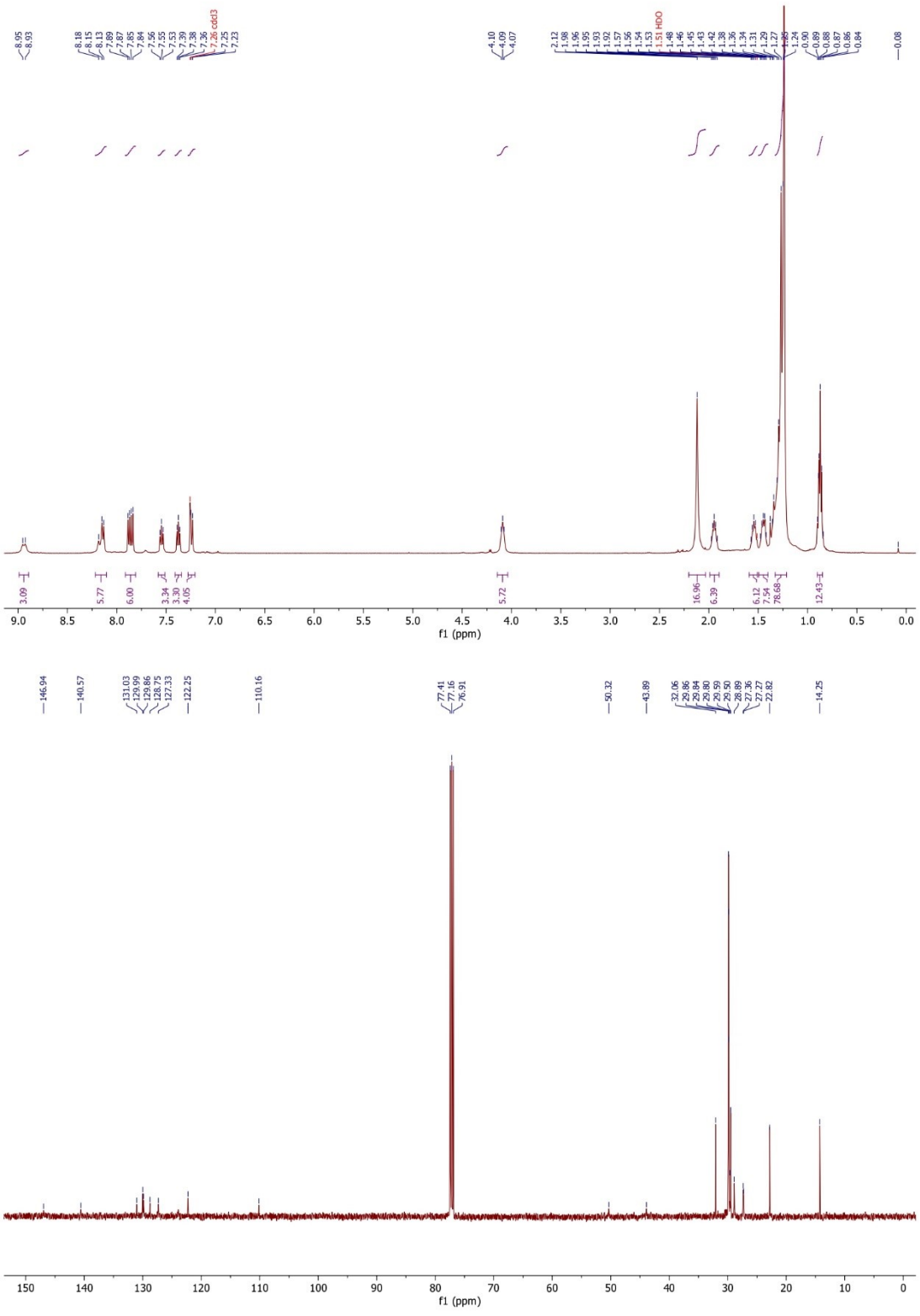

Figure S23. **^{1}H at 40°C and ^{13}C NMR spectra for compound 4 in $CDCl_3$.**

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 300.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

153 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-150 H: 0-200 N: 1-3 O: 1-3

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
1541.1998	1541.1990	0.8	0.5	33.5	C108 H154 N3 O3	298.3	n/a	n/a	108	154	3	3

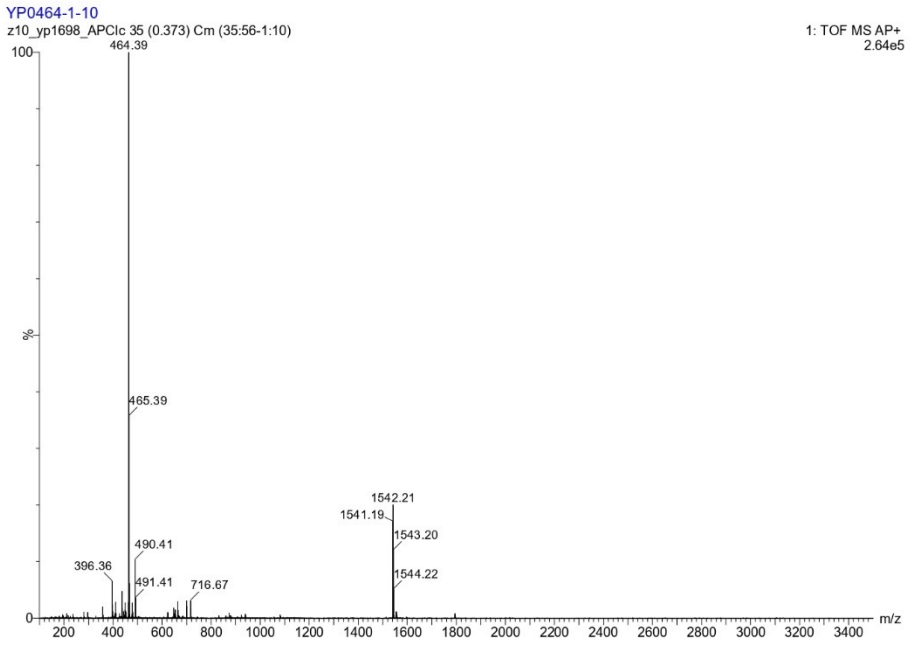

Figure S24. HRMS report for compound **4**.

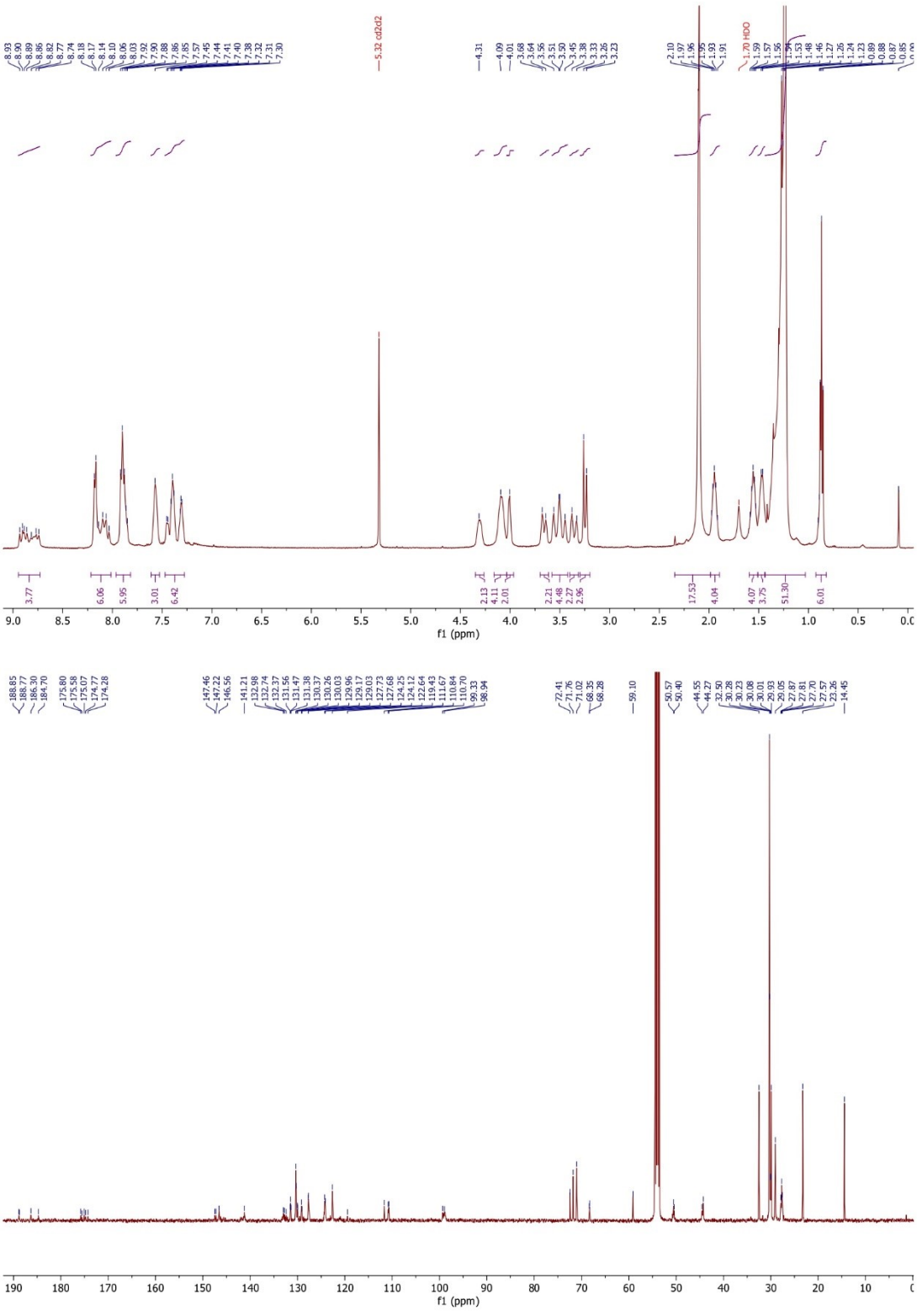

Figure S25. **^{1}H and ^{13}C NMR spectra for compound 5 in CD_2Cl_2.**

Single Mass Analysis

Tolerance = 15.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

71 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-100 H: 0-200 N: 2-4 O: 4-6

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
1435.0117	1435.0116	0.1	0.1	33.5	C97 H132 N3 O6	252.6	n/a	n/a	97	132	3	6

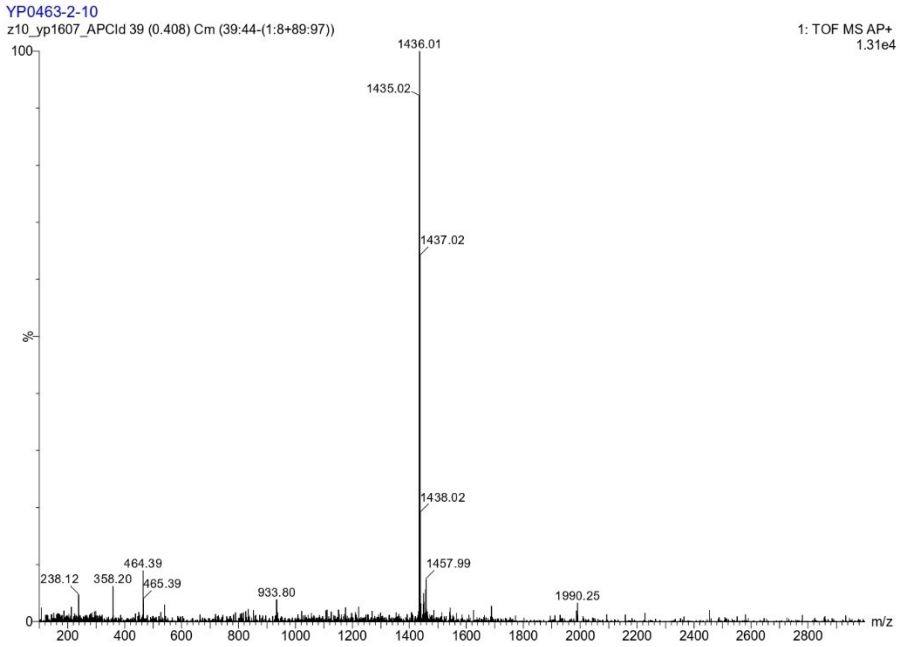

Figure S26. HRMS report for compound **5**.

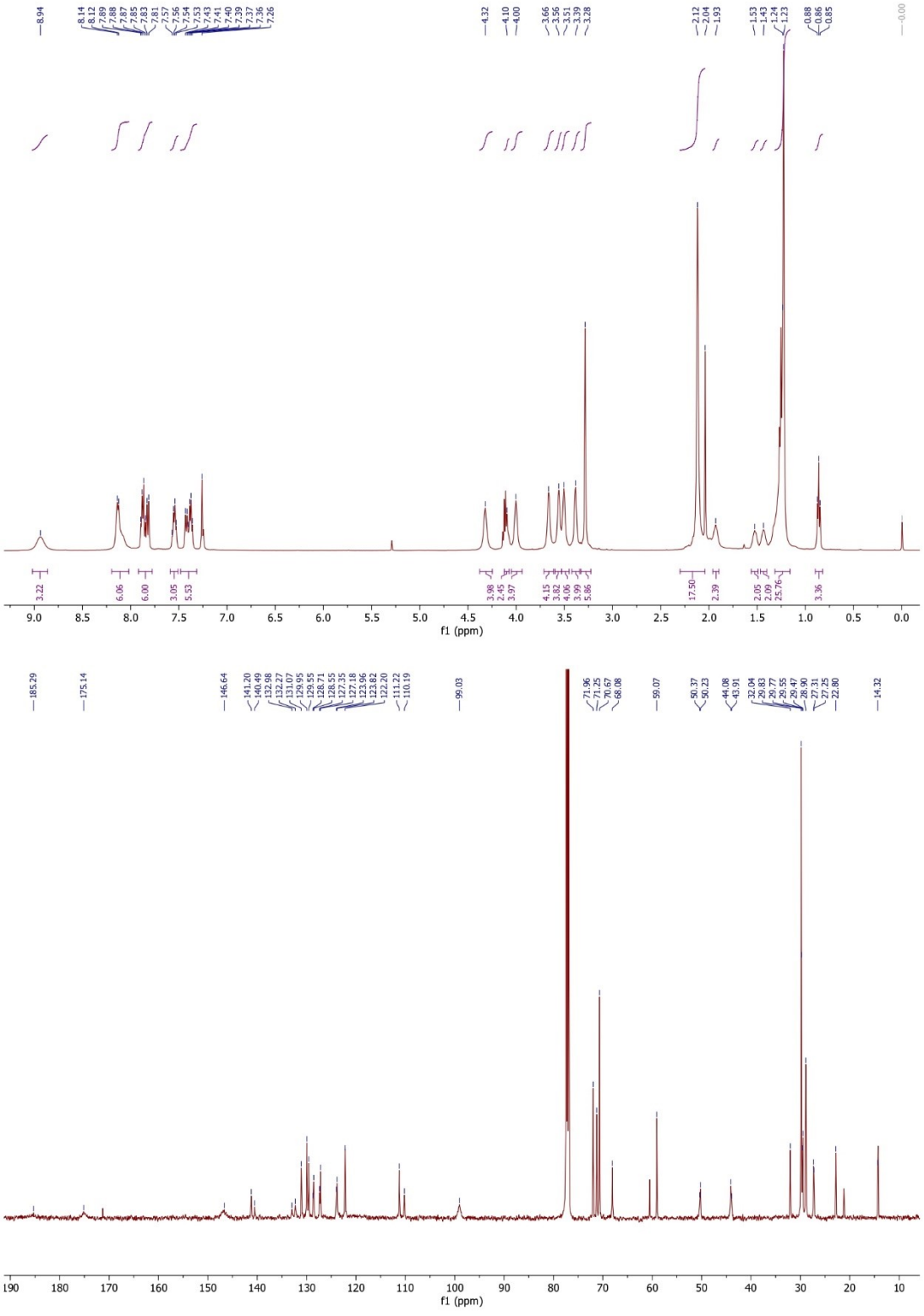

Figure S27. **^{1}H and ^{13}C NMR spectra for compound 6 in $CDCl_3$.**

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
30 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
1328.8224	1328.8242	-1.8	-1.4	33.5	C86 H110 N3 O9	292.0	n/a	n/a	86	110	3	9

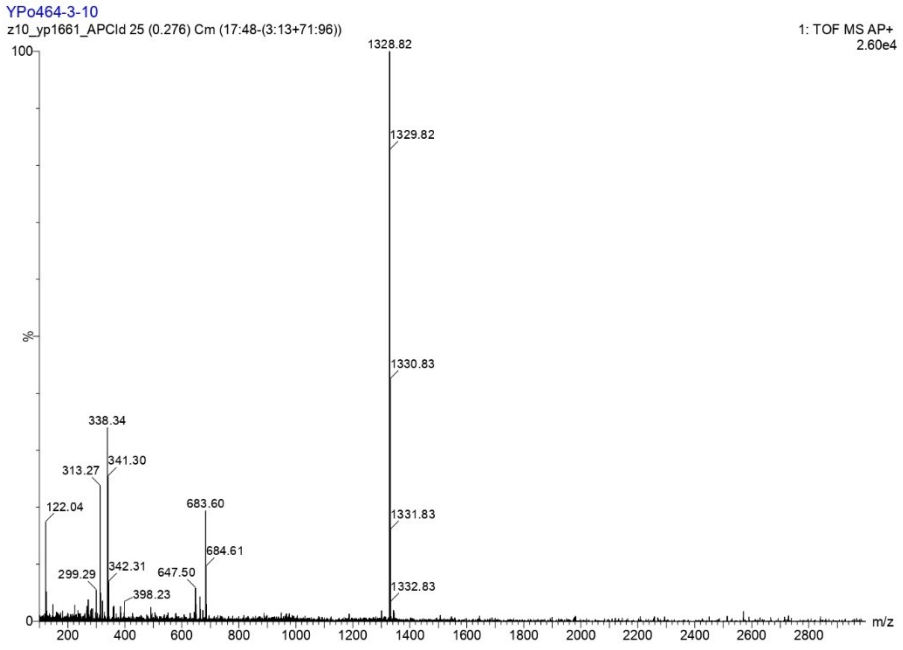

Figure S28. HRMS report for compound **6**.

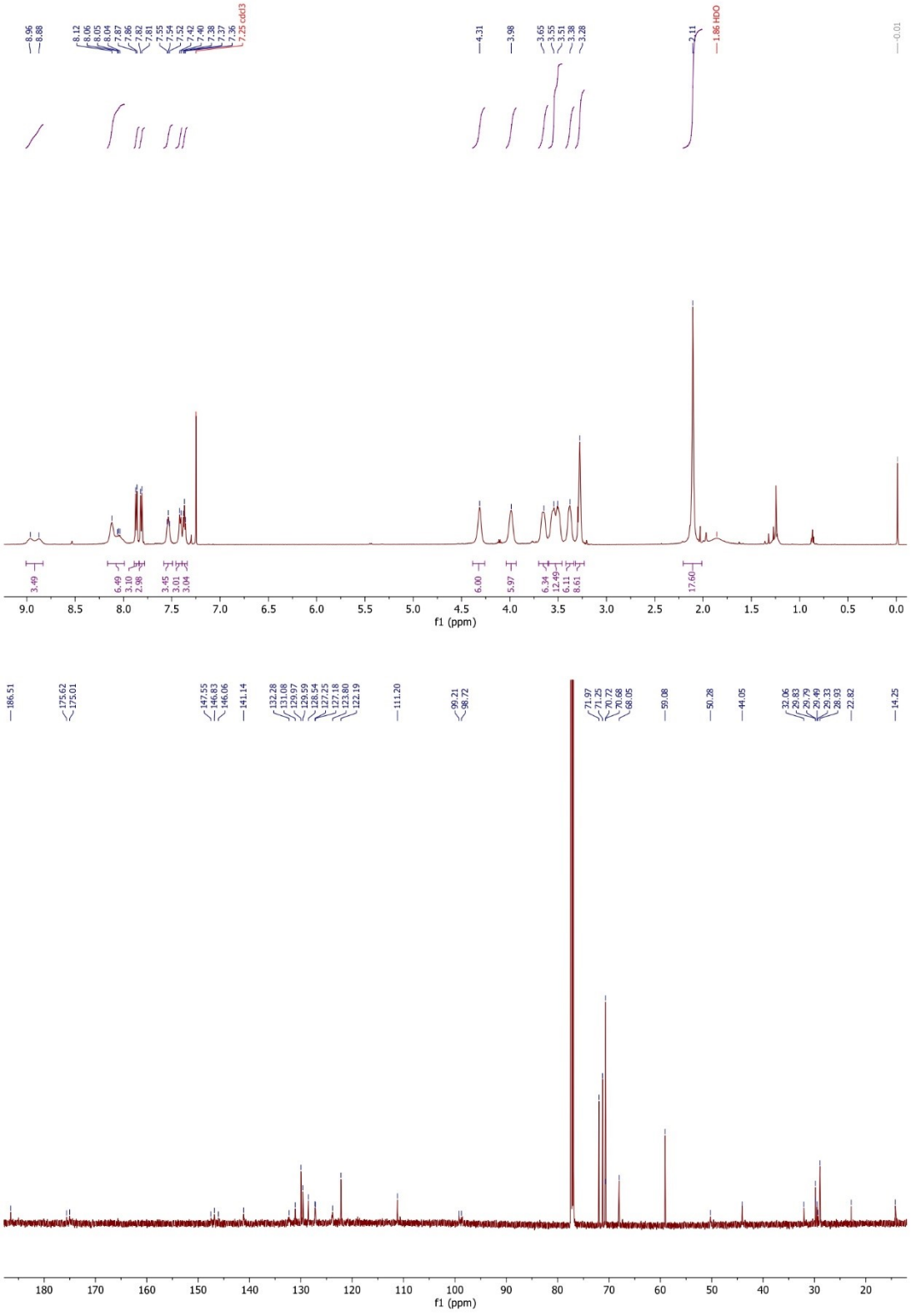

Figure S29. **^{1}H and ^{13}C NMR spectra for compound 7 in $CDCl_3$.**

Single Mass Analysis
Tolerance = 3.0 mDa / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Even Electron Ions
40 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O
1222.6393	1222.6368	2.5	2.0	33.5	C75 H88 N3 O12	368.1	n/a	n/a	75	88	3	12

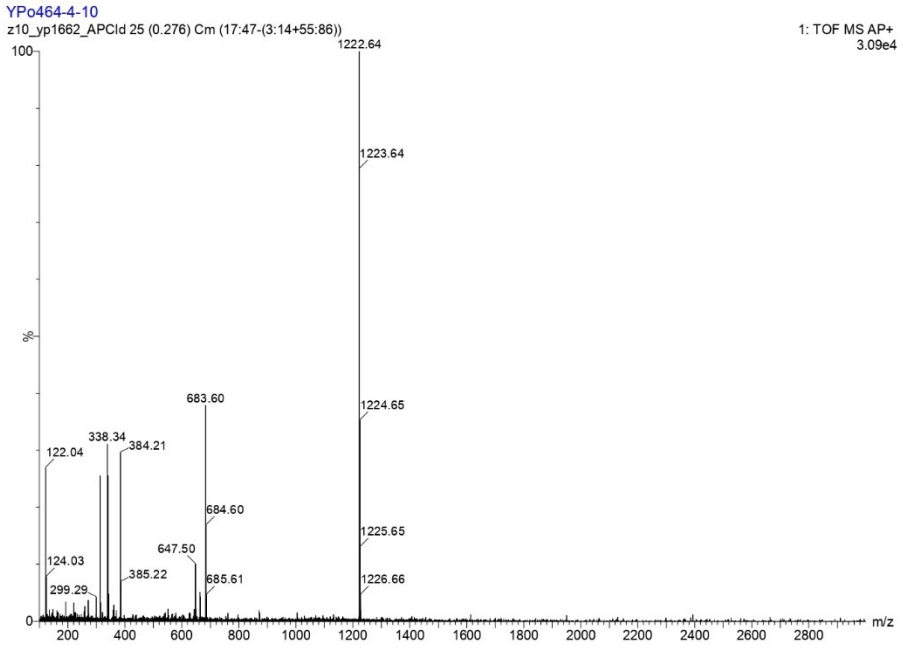

Figure S30. HRMS report for compound **7**.

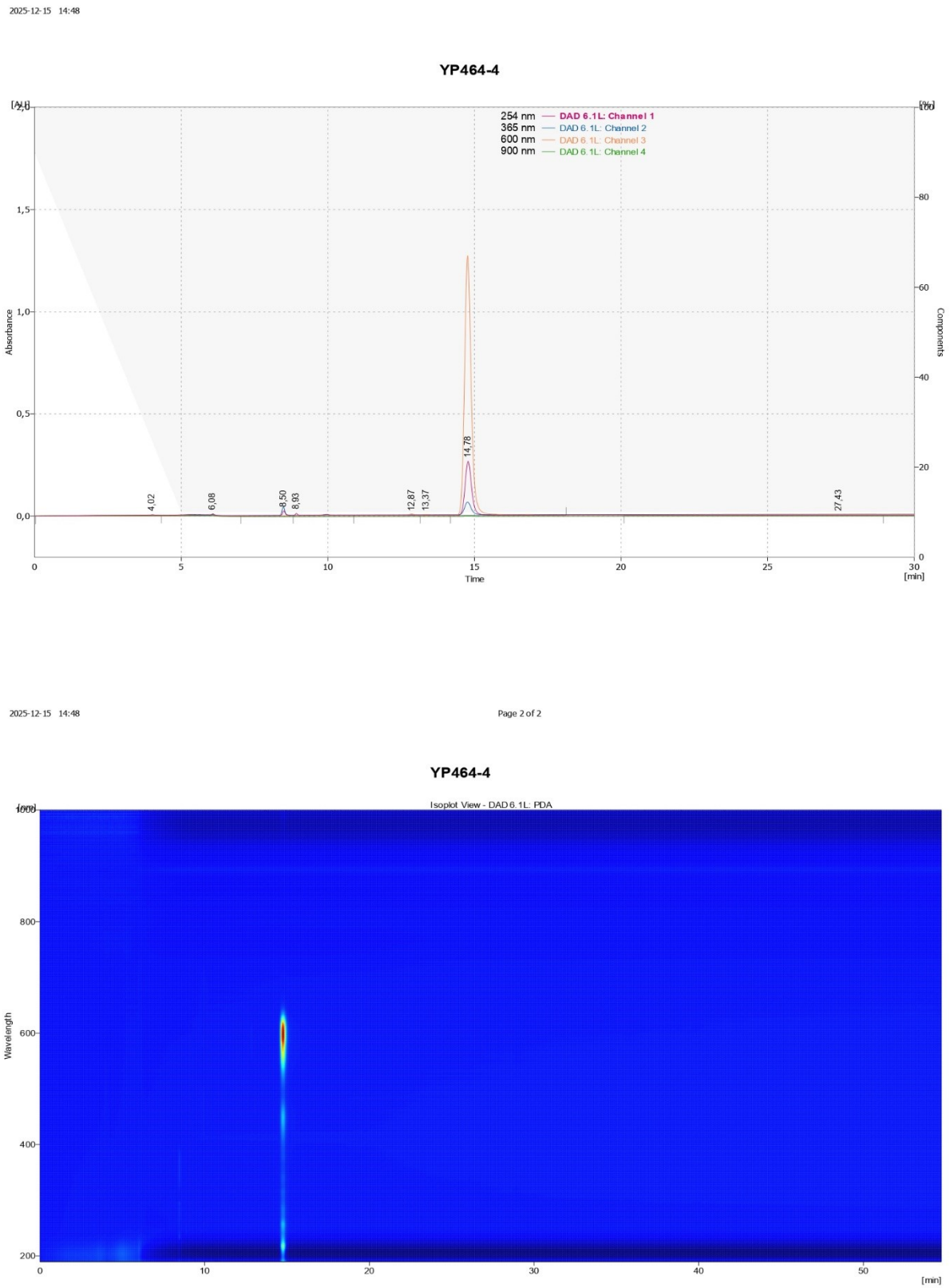

Figure S31. HPLC report for compound **7**. Method: 10% H_2O/HCO_2H 0.03% vol. 90% CH_3CN (Kromasil Eternity C18).

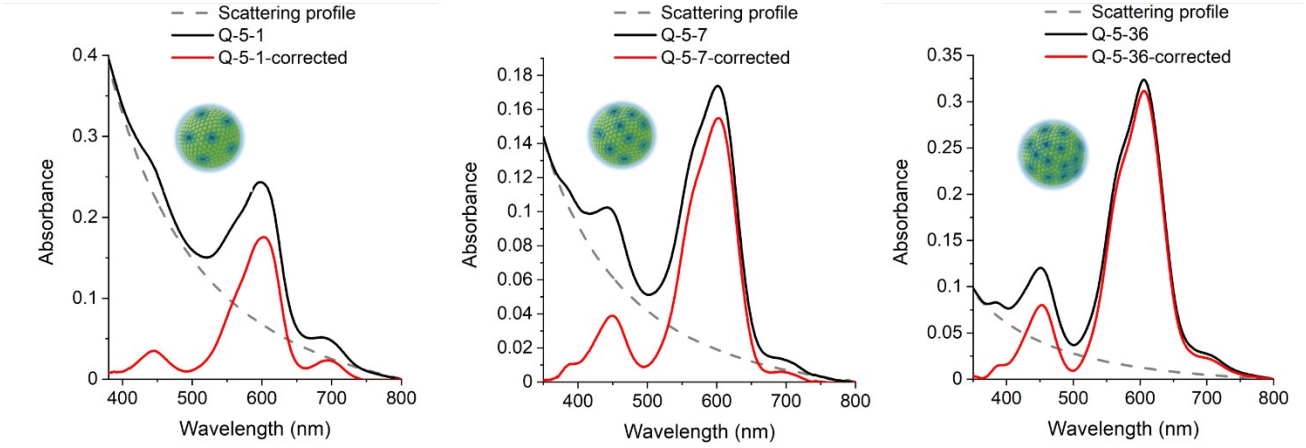

Figure S32. **Baseline corrections of measured absorbance spectra of 5-loaded QS** (solid black line), through the subtraction of the absorbance of blank QS (dashed grey line) to account for scattering contributions, yielding corrected absorbance spectra of Q-5 nanovesicle dispersions (solid red line).

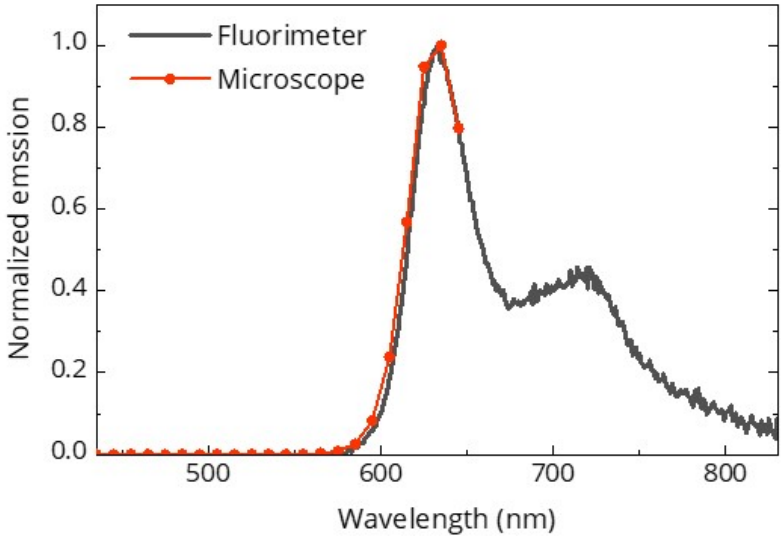

Figure S33. **Normalized emission spectra obtained using a fluorimeter (black) and microscope (red) from the Q-5-1 suspension**. The ratio between the two reported emission spectra was employed to estimate the scaling factor (S) used for calculating the σ2.

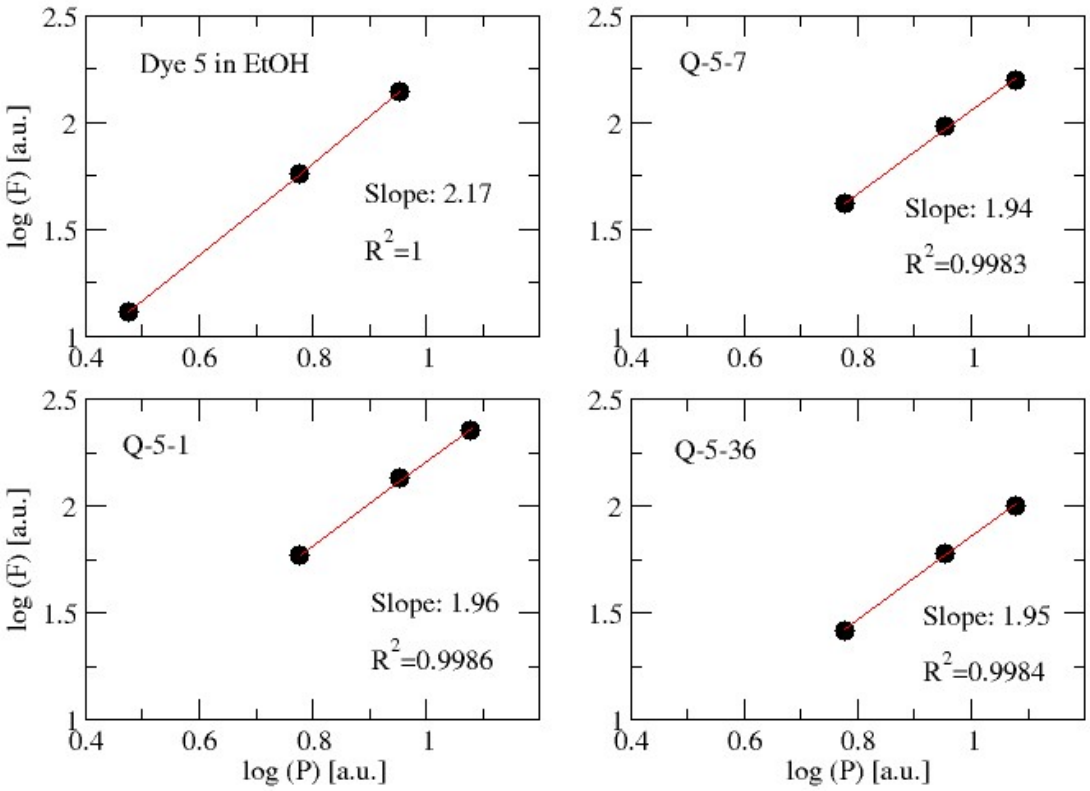

Figure S34. Log–log plots of the two-photon-excited fluorescence intensity (F) as a function of the laser power (P) are shown. The fluorescence intensity was collected at 1100 nm.

Table S1. **Description of dye-loaded QS**. In the table, it indicates the membrane components and their amounts, as well as the initial dye and membrane components concentration. Moreover, there is a description of the organic phase, and the dispersant media used.

Sample name		Membrane components			$Dye_{initial}$	Organic phase	Dispersant media
		Sterol	Surfactant	CHOL-PEG2000			
	**Q-5-1**	Chol 2.5 mM	MKC 2.5 mM	0.15 mM	2µM dye **5**	DMSO (2% v/v) EtOH (8% v/v)	PBS 100 mM
	**Q-5-7**	Chol 2.5 mM	MKC 2.5 mM	0.15 mM	10µM dye **5**	DMSO (2% v/v) EtOH (8% v/v)	PBS 100 mM
	**Q-5-36**	Chol 2.5 mM	MKC 2.5 mM	0.15 mM	50µM dye **5**	DMSO (2% v/v) EtOH (8% v/v)	PBS 100 mM
	**Q**	Chol 2.5 mM	MKC 2.5 mM	0.15 mM	-	DMSO (2% v/v) EtOH (8% v/v)	PBS 100 mM
	**Q-4**	Chol 2.5 mM	MKC 2.5 mM	0.15 mM	10µM dye **4**	DMSO (2% v/v) EtOH (8% v/v)	PBS 100 mM
	**Q-6**	Chol 2.5 mM	MKC 2.5 mM	0.15 mM	10µM dye **6**	DMSO (2% v/v) EtOH (8% v/v)	PBS 100 mM
	**Q-7**	Chol 2.5 mM	MKC 2.5 mM	0.15 mM	10µM dye **7**	DMSO (2% v/v) EtOH (8% v/v)	PBS 100 mM

Table S2. Quantities used for the preparation of dye-loaded QS using the DELOS-SUSP process.

Sample name		Membrane components			$Dye_{initial}$	Organic phase	Dispersant media (PBS)
		Sterol (cholesterol)	Surfactant (MKC)	CHOL-PEG2000			
	**Q-5-1**	26.99 mg	26.4 mg	5.16 mg	0.08 mg	0.576 mL DMSO 2.304 mL EtOH	25.92 mL
	**Q-5-7**	27.36 mg	26.64 mg	5.04 mg	0.42 mg	0.576 mL DMSO 2.304 mL EtOH	25.92 mL
	**Q-5-36**	27.03 mg	26.56 mg	5.19 mg	2.08 mg	0.576 mL DMSO 2.304 mL EtOH	25.92 mL
	**Q**	27.29 mg	26.67 mg	5.06 mg	-	0.576 mL DMSO 2.304 mL EtOH	25.92 mL
	**Q-4**	27.04 mg	26.52 mg	5.14 mg	0.434 mg	0.576 mL DMSO 2.304 mL EtOH	25.92 mL
	**Q-6**	27.3 mg	26.41 mg	5.22 mg	0.390 mg	0.576 mL DMSO 2.304 mL EtOH	25.92 mL
	**Q-7**	27.26 mg	26.69 mg	5.34 mg	0.350 mg	0.576 mL DMSO 2.304 mL EtOH	25.92 mL

Table S3. Physicochemical and spectroscopical characterization of quatsomes loaded with dyes 4, 5, 6, and 7. In the table, it is indicated the experimental concentrations of fluorophore and membrane components, as well as the % of dye loading and the % of dye retention.

	 Q-4	 Q-5	 Q-6	 Q-7
$[Dye]_{exp}$ (μM)[a]	8.4 ± 0.3	7.2 ± 0.4	2.04 ± 0.06	2.3 ± 0.1
$[membrane\ components]_{exp}$ (mg/mL)[b]	1.23 ±	1.4 ± 0.1	0.29 ±	0.39 ±
Dye loading (%w/w)[c]	1.06 ±	0.76 ± 0.07	0.94 ±	0.71 ±
Dye retention (%)[d]	86	71	20	23

[a]Calculated from absorbance values (Lambert-Beer Law); [b]Calculated from gravimetric analysis; [c]Loading = (mass dye)/ (mass weighted-mass dye); where dye mass was obtained from absorbance (Lambert-Beer Law) and the total mass from gravimetric analysis; [d]Dye retention = ($[Dye]_{exp}$/ $[Dye]_{theo}$) x 100.

Table S4. Exponential components analysis obtained from reconvolution fits of bi-exponential emission decays.

	t_1(ns)	B_1	t_2(ns)	B_2	<t> (ns)*	χ^2
QS-5-1/0.12	0.81	0.0314	2.11	0.0008	0.89	0.79
QS-5-7/0.76	0.80	0.0313	2.38	0.0005	0.87	0.80
QS-5-36/3.86	0.79	0.0296	2.46	0.0007	0.91	0.98

**Average lifetime:* $\langle t \rangle = \frac{B_1 t_1^2 + B_2 t_2^2}{B_1 t_1 + B_2 t_2}$

Table S5. Geometric parameters of dye-loaded QS.

	Q-5-1	Q-5-7	Q-5-36
Outer diameter (nm)[a]	119	110	142
Thickness membrane (nm)[b]	4.7	4.7	4.7
Inner diameter (nm)	109.6	100.6	132.6
Volume vesicles exterior (nm^3)	$8.8x10^5$	$6.9x10^5$	$1,5x10^6$
Volume vesicles interior (nm^3)	$6.9x10^5$	$5.3x10^5$	$1,2x10^6$
Volume membrane (nm^3)	$1,9x10^5$	$1.6x10^5$	$2.8x10^5$
Volume membrane (dm^3)	$1,9x10^{-19}$	$1.6x10^{-19}$	$2.8x10^{-19}$
Surface outer membrane (nm^3)	$4.5x10^4$	$3.8x10^4$	$6.3x10^4$
Surface inner membrane (nm^2)	$3.8x10^4$	$3.2x10^4$	$5.5x10^4$
Surface synthon (nm^2)[c]	0.57	0.57	0.57
nº synthons at the outer QS membrane	$7.8x10^4$	$6.7x10^4$	$1.1x10^5$
nº synthons at the inner membrane	$6.6x10^4$	$5.6x10^4$	$9.7x10^4$
nº synthons per 1 QS	**$1.4x10^5$**	**$1.2x10^5$**	**$2.1x10^5$**

[a]Average size obtained with DLS measurements; [b]Based on previous AFM-FS experiments performed with other QS formulations, prepared using another ammonium quaternary surfactant[1,2]; [c]Based on Molecular Dynamics simulations performed with other Qs formulations (as explained before) [1,2].

Table S6. **Calculation of the number of dye molecules per QS.**

	Q-5-1	**Q-5-7**	**Q-5-36**
$[Dye]_{exp}$ (mols/mL)[a]	1.1×10^{-9}	7.2×10^{-9}	3.6×10^{-8}
Dye molecules/mL	6.3×10^{14}	4.4×10^{15}	2.2×10^{16}
nº QS per ml[b]	6.5×10^{12}	6.1×10^{12}	3.3×10^{12}
mol QS per mL	1.1×10^{-8}	1.1×10^{-8}	5.5×10^{-9}
number of dye molecules/QS[c]	**98**	**718**	**6531**

[a]Calculated from absorbance values (Lambert-Beer Law); [b]Calculated as mass of membrane components (calculated from gravimetric analysis/mass of 1 QS; [c]Calculated as (number of dye molecules/mL)/(number of QS/mL).

Table S7. Brightness one-photon and two-photon per particle calculations.

	Q-5-1	Q-5-7	Q-5-36
ε (M^{-1} cm^{-1})[a]	$2.2x10^5$	$2.2x10^5$	$2.2x10^5$
ε per particle, ε_p (M^{-1} cm^{-1})[b]	$2.1x10^7$	$1.6x10^8$	$1.4x10^9$
ϕF (%)[c]	23	8	3
Brightness one-photon (M-1 cm-1)[d]	**$5x10^4$**	**$1.7x10^4$**	**$6.5\ x10^3$**
Brightness one-photon per particle (M-1 cm-1)[e]	**$4.9x10^6$**	**$1.2x10^7$**	**$4.3x10^7$**
σ_2 (GM)[f]	800	600	300
σ_2 per particle (GM)[g]	98	718	6531
Brightness two-photon (GM)[h]	**184**	**48**	**9**
Brightness two-photon per particle (GM)[i]	**$1.8x10^4$**	**$3.4x10^4$**	**$5.9x10^4$**

[a]Molar extinction coefficient. [B]ε_p is the molar extinction coefficient at the maximum absorption wavelength (605 nm) of a single QS, calculated as ε × n (n is the estimated number of fluorophores per vesicle). [c]Fluorescence quantum yield. [d]Brightness one-photon = $\phi_F \times \varepsilon$. [e]Brightness one-photon of a single fluorescent QS calculated as $\varepsilon_p \times \phi_F$. [f]Two-photon cross section. [g]σ_2 per particle is the two-photon cross section of a single QS at the maximum two-photon absorption wavelength (910nm), calculated as $\sigma_2 \times$ n (n is the estimated number of fluorophores per vesicle). [h]Brightness two-photon= $\phi_F \times \sigma_2$. [i]Brightness two-photon of a single fluorescent QS calculated as $\sigma_{2p} \times \phi_F$, where ϕ_F is the fluorescence quantum yield and σ_{2p} is the two-photon cross section of a single QS at the maximum two-photon absorption wavelength (910nm), calculated as $\sigma_2 \times$ n (n is the estimated number of fluorophores per vesicle.

Table S8. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the simplified single-arm chromophore (transoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

C	2.4400110	0.8669430	-0.3869330
C	2.5667660	-0.4716730	-0.1075250
C	3.8522300	-1.0399790	0.0725770
C	4.9807870	-0.1699110	-0.0396170
C	4.7883100	1.2065160	-0.3186280
C	3.5394610	1.7383040	-0.4928240
C	0.2833430	0.1234830	-0.3311410
H	5.6625230	1.8459630	-0.3907670
H	3.4090600	2.7943260	-0.6961280
C	4.0960480	-2.4120430	0.3559620
C	6.2852470	-0.6969790	0.1340630
C	6.4819110	-2.0223400	0.4054250
C	5.3699190	-2.8857600	0.5163360
H	3.2634700	-3.0974410	0.4465750
H	7.1310960	-0.0214920	0.0460550
H	7.4851110	-2.4135400	0.5356830

H	5.5279540	-3.9374960	0.7315950
N	1.0839970	1.2015190	-0.5405680
C	0.6123110	2.5444850	-0.8434070
H	1.3850660	3.0415630	-1.4350720
H	-0.2645480	2.4579440	-1.4892120
C	0.2812590	3.3622630	0.4033640
H	1.1783350	3.4433160	1.0290520
H	-0.4670170	2.8229100	0.9938690
C	1.1775860	-1.0930730	-0.0494940
C	0.9999850	-2.1540440	-1.1546040
H	1.7168780	-2.9659230	-1.0243400
H	-0.0021260	-2.5836840	-1.1414130
H	1.1702110	-1.7139870	-2.1399250
C	0.8853330	-1.6586330	1.3545460
H	-0.1192830	-2.0776030	1.4175390
H	1.5963270	-2.4467260	1.6060210
H	0.9755610	-0.8747520	2.1100210
C	-3.3526760	-0.8565080	-0.2186750
C	-1.9694270	-0.8633620	-0.2010240

H	-1.5634420	-1.8541740	-0.0274390
C	-1.0917360	0.2159940	-0.3748190
H	-1.5475480	1.1801310	-0.5447790
C	-6.2143070	-0.9554190	0.2825490
C	-5.5123830	-2.2559580	-0.0139810
C	-3.9907530	-2.1649420	0.0053790
C	-4.1415540	0.3562970	-0.4244950
C	-5.6640580	0.2335560	-0.4633620
O	-3.3495600	-3.1884420	0.1939390
O	-3.6557600	1.4698820	-0.5861260
O	-7.1470460	-0.8733480	1.0490790
H	-5.7960470	-2.5692430	-1.0285780
H	-5.8355400	-3.0362460	0.6753260
H	-5.9449740	0.1285310	-1.5207710
H	-6.1059100	1.1584410	-0.0924310
C	-0.2417280	4.7537510	0.0556730
H	0.5006330	5.2811190	-0.5569100
H	-1.1395120	4.6549060	-0.5657440
C	-0.5669970	5.5845400	1.2927200

H	-0.9409020	6.5743350	1.0192690
H	-1.3325990	5.0963680	1.9027880
H	0.3188300	5.7240390	1.9201640

Table S9. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the simplified single-arm chromophore (cisoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

C	-1.5573750	0.2571040	-0.7260600
C	-2.2815130	-0.2709720	0.3122960
C	-3.6246980	-0.6718200	0.1106730
C	-4.1724280	-0.5069030	-1.1982000
C	-3.3738420	0.0371510	-2.2364310
C	-2.0778200	0.4210700	-2.0223540
C	-0.0792570	0.2494220	0.9897990
H	-3.8130030	0.1443890	-3.2232620
H	-1.4778940	0.8287620	-2.8264520
C	-4.4553190	-1.2297110	1.1196500
C	-5.5132490	-0.8970410	-1.4414890
C	-6.2861290	-1.4274380	-0.4458920
C	-5.7461690	-1.5946400	0.8483470
H	-4.0614560	-1.3721930	2.1179880

H	-5.9167400	-0.7664570	-2.4412430
H	-7.3106530	-1.7225560	-0.6453540
H	-6.3617660	-2.0191350	1.6346420
N	-0.2570450	0.5949540	-0.2897700
C	-1.3931290	-0.3125750	1.5396440
C	-1.9305390	0.5704440	2.6801090
H	-2.8908060	0.1949800	3.0369490
H	-1.2406330	0.5753570	3.5269250
H	-2.0768120	1.6005090	2.3459610
C	-1.1238410	-1.7517270	2.0175330
H	-0.4333070	-1.7419570	2.8639970
H	-2.0498430	-2.2390660	2.3287800
H	-0.6677240	-2.3379960	1.2177480
C	3.1864910	-0.1858570	0.4824980
C	2.4213110	0.3621510	1.5181270
H	3.0483310	0.7683660	2.3108430
C	1.0561130	0.3944180	1.7898400
H	0.8180490	0.5135030	2.8436270
C	5.0449680	-1.8991610	-0.9738600

C	5.5703880	-0.6016170	-0.4176860
C	4.6337010	0.0671290	0.5835660
C	2.6532610	-1.1479050	-0.4638900
C	3.6108560	-1.8400100	-1.4340910
O	5.1186740	0.8104140	1.4232220
O	1.4642560	-1.4572750	-0.5259090
O	5.7170730	-2.9023830	-1.0521180
H	5.6958560	0.0991670	-1.2550390
H	6.5461380	-0.7437660	0.0467160
H	3.5846930	-1.2683840	-2.3725750
H	3.2349290	-2.8408870	-1.6473220
C	0.6711400	1.3333490	-1.1384690
H	0.7018750	0.8287840	-2.1070710
H	1.6646620	1.2516980	-0.7061240
C	0.2841330	2.8045810	-1.2996120
H	-0.7252110	2.8853040	-1.7193810
H	0.9615640	3.2341970	-2.0475290
C	0.3680020	3.6221080	-0.0121310
H	-0.2996630	3.1891800	0.7411730

H	1.3800940	3.5452740	0.4008950
C	0.0066530	5.0878740	-0.2304650
H	-1.0136220	5.1915280	-0.6131360
H	0.0719440	5.6565100	0.7005170
H	0.6800190	5.5576380	-0.9541530

Table S10. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the three-arm chromophore (transoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

C	1.4387290	0.4790590	-0.0758250
C	0.3405740	1.4487230	-0.1732510
C	-1.0760300	1.0112690	-0.1802640
C	-1.3683080	-0.4266660	-0.1226840
C	-0.2830840	-1.4320110	-0.0369070
C	1.1081730	-0.9638070	-0.0010230
O	-1.9811580	1.8529680	-0.2365690
O	2.6229300	0.8414310	-0.0511710
O	-0.5616190	-2.6383630	0.0024370
C	-2.6407690	-0.9387300	-0.1435690
C	-3.8763450	-0.2528890	-0.2221830
H	-2.6483150	-2.0214870	-0.0942950

C	-5.1042080	-0.8570370	-0.2288820
H	-3.8164860	0.8238140	-0.2756770
C	-5.4728490	-2.3451680	-0.1090510
N	-6.2685070	-0.1402900	-0.3441730
C	-7.3869950	-0.9758280	-0.2635950
C	-6.9960100	-2.2882990	-0.1356910
C	-8.7380590	-0.5816290	-0.3020290
C	-7.9689830	-3.3138260	-0.0542420
C	-9.3455150	-2.9292200	-0.1002470
C	-9.6911970	-1.5604140	-0.2211180
H	-10.7433000	-1.2934860	-0.2459970
H	-9.0200380	0.4612400	-0.3843250
C	-4.9658440	-2.9176710	1.2290910
H	-5.3353950	-2.3192380	2.0650170
H	-3.8763340	-2.9258190	1.2731220
H	-5.3182630	-3.9407330	1.3701750
C	-4.9276670	-3.1307780	-1.3186140
H	-5.2714510	-2.6811320	-2.2530570
H	-5.2780410	-4.1641340	-1.2972150

H	-3.8371920	-3.1430410	-1.3283170
C	-6.3382590	1.3025220	-0.4871460
H	-5.5067180	1.6201420	-1.1215610
H	-7.2541650	1.5416850	-1.0343710
C	-7.6728770	-4.7001070	0.0694460
C	-8.6698790	-5.6345040	0.1423770
C	-10.0280330	-5.2490060	0.0978010
C	-10.3505330	-3.9258160	-0.0205690
H	-6.6413890	-5.0254040	0.1057820
H	-8.4143670	-6.6851500	0.2358110
H	-10.8066650	-6.0018910	0.1571920
H	-11.3903470	-3.6136710	-0.0563990
C	2.1866070	-1.8085630	0.0869190
C	2.1958860	-3.2196950	0.1832180
H	3.1311140	-1.2759630	0.0806870
C	3.3170620	-4.0043060	0.2049300
H	1.2265270	-3.6915860	0.2218930
N	3.2415050	-5.3689550	0.3185830
C	4.5100800	-5.9527980	0.2466680

C	5.4772230	-4.9815630	0.1266870
C	4.7995310	-3.6163420	0.0954670
C	5.0672460	-2.8948720	-1.2396410
H	4.7280380	-3.5059970	-2.0792160
H	6.1343390	-2.7087290	-1.3720460
H	4.5474660	-1.9372330	-1.2852420
C	5.2168990	-2.7600400	1.3077320
H	4.9844830	-3.2783640	2.2409190
H	4.6995280	-1.7998530	1.3140370
H	6.2908130	-2.5661740	1.2922630
C	4.8099950	-7.3278020	0.2860250
C	6.1259820	-7.6966360	0.2144580
C	7.1638520	-6.7384270	0.1023210
C	6.8435980	-5.3456210	0.0551420
H	4.0285150	-8.0743950	0.3617680
H	6.3944340	-8.7483330	0.2403160
C	1.9974910	-6.1072150	0.4544240
H	1.3521540	-5.5438970	1.1316480
H	2.2188910	-7.0551630	0.9517410

C	8.5203300	-7.1441210	0.0325800
C	9.5288630	-6.2277400	-0.0773590
C	9.2180610	-4.8506020	-0.1231150
C	7.9200320	-4.4221830	-0.0596480
H	8.7434460	-8.2065800	0.0691260
H	10.5629170	-6.5512780	-0.1292550
H	10.0191680	-4.1235680	-0.2099000
H	7.7121750	-3.3607660	-0.0966870
C	0.5352140	2.8053410	-0.2464860
C	1.7557800	3.5203330	-0.2709370
H	-0.3985540	3.3551260	-0.2916730
C	1.8758700	4.8833890	-0.2831470
H	2.6500520	2.9170170	-0.2589540
N	3.1003470	5.5004290	-0.3227020
C	0.7942050	5.9732780	-0.2374750
C	1.6380070	7.2427580	-0.2165110
C	2.9675370	6.8907410	-0.2568850
C	-0.0435530	5.8431810	1.0493590
H	0.6035040	5.8548970	1.9294790

H	-0.6140310	4.9138020	1.0600630
H	-0.7454480	6.6738810	1.1401540
C	-0.0809980	5.9070870	-1.5049660
H	0.5392830	5.9699330	-2.4020770
H	-0.7887090	6.7375800	-1.5298010
H	-0.6484350	4.9766600	-1.5484700
C	4.3675330	4.7923350	-0.3840340
H	4.2431840	3.9529830	-1.0713750
H	5.1063150	5.4588070	-0.8368130
C	1.2665560	8.6080190	-0.1658080
C	4.0088080	7.8380090	-0.2320600
C	3.6666000	9.1620660	-0.1793370
C	2.3135420	9.5817850	-0.1484410
C	1.9829740	10.9593100	-0.0969960
C	0.6808160	11.3744880	-0.0654310
C	-0.3572640	10.4167460	-0.0838490
C	-0.0758840	9.0784770	-0.1318930
H	5.0487840	7.5344900	-0.2453410
H	4.4433530	9.9203350	-0.1572120

H	-1.3908270	10.7469700	-0.0594780
H	-0.8918150	8.3676580	-0.1454980
H	2.7922410	11.6837770	-0.0836650
H	0.4412540	12.4317280	-0.0267610
C	-6.3034060	2.0466470	0.8468130
H	-5.3973250	1.7574190	1.3895970
H	-7.1546370	1.7256060	1.4595870
C	1.2980430	-6.3531680	-0.8833140
H	1.1662080	-5.3917900	-1.3899960
H	1.9577730	-6.9567800	-1.5169510
C	-0.0617760	-7.0407280	-0.7419790
H	-0.4435570	-7.2422420	-1.7485080
H	0.0676640	-8.0222980	-0.2675840
C	-1.0954580	-6.2230430	0.0339770
H	-1.1638660	-5.1983710	-0.3438020
H	-2.0852560	-6.6824320	-0.0381490
H	-0.8502800	-6.1572630	1.0978990
C	-6.3330260	3.5616760	0.6635230
H	-7.2286770	3.8446620	0.0955910

H	-5.4737480	3.8655280	0.0540360
C	-6.3097430	4.3154390	1.9893440
H	-5.4071790	4.0768070	2.5596720
H	-6.3293050	5.3972430	1.8335640
H	-7.1725910	4.0522980	2.6092020
C	4.8493650	4.3071380	0.9840800
H	5.0036740	5.1791130	1.6297960
H	4.0539730	3.7111050	1.4428310
C	6.1312100	3.4738800	0.9176650
H	6.9433410	4.0780880	0.4926060
H	6.4356830	3.2417740	1.9437710
C	5.9873380	2.1716340	0.1286070
H	5.1131760	1.5989860	0.4530320
H	5.8719020	2.3536120	-0.9437420
H	6.8743420	1.5441470	0.2527750

Table S11. Cartesian coordinates (Å) and atom labels for the S_0-optimized geometry of the three-arm chromophore (cisoid conformer) obtained at the CAM-B3LYP/6-31G(d,p) DFT level.

C	-1.0530680	0.6053750	-0.4541650
C	-0.2512420	1.8225810	-0.3464590

C	1.2427630	1.7104610	-0.2897320
C	1.8539980	0.3833980	-0.1381260
C	1.0381400	-0.8491780	-0.1206260
C	-0.4069740	-0.7207850	-0.3258200
O	1.9497320	2.7219610	-0.3443580
O	-2.2706830	0.6670990	-0.6574440
O	1.5783530	-1.9514130	0.0471660
C	3.2055510	0.1891580	0.0022510
C	4.2535850	1.1391330	0.0227550
H	3.4553290	-0.8594920	0.1147180
C	5.5796960	0.8303510	0.1651930
H	3.9608720	2.1720480	-0.0886910
C	6.2669440	-0.5403440	0.2830500
N	6.5514420	1.7969490	0.2149300
C	7.8265590	1.2287210	0.3022280
C	7.7366000	-0.1425170	0.3578690
C	9.0551700	1.9155990	0.3314590
C	8.9105350	-0.9267750	0.4673180
C	10.1655390	-0.2425050	0.5065960

C	10.1996730	1.1721820	0.4337830
H	11.1654810	1.6675860	0.4575540
H	9.0999320	2.9961820	0.2668080
C	5.9896980	-1.3898790	-0.9727600
H	6.2775010	-0.8440800	-1.8742770
H	4.9336750	-1.6487460	-1.0552620
H	6.5647310	-2.3169050	-0.9466720
C	5.8209980	-1.2537290	1.5752780
H	5.9919170	-0.6135190	2.4438840
H	6.3884010	-2.1741730	1.7229870
H	4.7614450	-1.5103050	1.5451760
C	6.3000010	3.2249050	0.1422120
H	5.3773580	3.4342650	0.6896080
H	7.1026700	3.7346490	0.6820200
C	8.9286470	-2.3476360	0.5416660
C	10.1058430	-3.0372770	0.6468280
C	11.3428740	-2.3564550	0.6839240
C	11.3643720	-0.9913160	0.6147510
H	7.9963010	-2.8964490	0.5159840

H	10.0893340	-4.1210250	0.7023240
H	12.2673620	-2.9177300	0.7671070
H	12.3077030	-0.4534640	0.6422550
C	-1.2561150	-1.7973110	-0.4084940
C	-0.9404580	-3.1728130	-0.3262510
H	-2.2882010	-1.5022960	-0.5608500
C	-1.8479230	-4.1973230	-0.3639510
H	0.1059760	-3.4055100	-0.2047960
N	-1.4578580	-5.5096020	-0.2957150
C	-2.5639940	-6.3655460	-0.2832790
C	-3.7292380	-5.6418070	-0.3888210
C	-3.3805960	-4.1594970	-0.4598920
C	-3.9739370	-3.3931160	0.7381710
H	-3.6197990	-3.8205530	1.6790680
H	-5.0635880	-3.4524330	0.7340490
H	-3.6909180	-2.3401250	0.7162400
C	-3.8140170	-3.5493030	-1.8078220
H	-3.3542010	-4.0900730	-2.6382430
H	-3.5231020	-2.5007870	-1.8825180

H	-4.8969080	-3.6101570	-1.9291800
C	-2.5438810	-7.7693390	-0.1788980
C	-3.7433020	-8.4281060	-0.1984250
C	-4.9731650	-7.7344030	-0.3176910
C	-4.9784580	-6.3078250	-0.4148030
H	-1.6133980	-8.3149990	-0.0774810
H	-3.7664470	-9.5106120	-0.1183260
C	-0.0742390	-5.9449280	-0.2078570
H	0.5126180	-5.3158350	-0.8803210
H	-0.0141310	-6.9628340	-0.6017280
C	-6.2032520	-8.4386240	-0.3388870
C	-7.3951600	-7.7787450	-0.4524430
C	-7.4058590	-6.3696960	-0.5503730
C	-6.2380970	-5.6566260	-0.5318160
H	-6.1787890	-9.5219370	-0.2631110
H	-8.3295340	-8.3294840	-0.4681900
H	-8.3523520	-5.8465520	-0.6416120
H	-6.2771520	-4.5779090	-0.6095040
C	-0.6903090	3.1280970	-0.3516600

C	-1.8027030	4.0316040	-0.2804690
H	0.2093830	3.7420700	-0.3549330
C	-3.1779370	4.1076070	-0.1834460
H	-1.3900790	5.0324910	-0.3106350
N	-3.7719140	5.3535180	-0.1936180
C	-4.3012830	3.0809330	0.0109300
C	-5.5081660	3.9671410	0.2823580
C	-5.1323170	5.2774350	0.1316860
C	-3.9861620	2.1746590	1.2109580
H	-3.9369280	2.7703470	2.1266280
H	-3.0438200	1.6590480	1.0583910
H	-4.7629400	1.4197570	1.3431050
C	-4.5416010	2.3384030	-1.3240350
H	-4.8328570	3.0566950	-2.0955550
H	-5.3587700	1.6221290	-1.2117150
H	-3.6480920	1.8039730	-1.6287710
C	-3.1158540	6.6263730	-0.4363080
H	-2.3260040	6.4677920	-1.1718920
H	-3.8465850	7.2862250	-0.9133280

C	-6.8546150	3.6454180	0.5802970
C	-6.0250870	6.3548570	0.2931790
C	-7.3262190	6.0631310	0.6021820
C	-7.7743200	4.7269060	0.7491950
C	-9.1291700	4.4462780	1.0584880
C	-9.5731880	3.1599170	1.1886760
C	-8.6706180	2.0877770	1.0109450
C	-7.3547130	2.3208310	0.7171830
H	-5.6996820	7.3830430	0.1893700
H	-8.0424690	6.8672270	0.7406600
H	-9.0261950	1.0670090	1.1085420
H	-6.6841090	1.4828030	0.5817160
H	-9.8127300	5.2806070	1.1875540
H	-10.6128900	2.9585790	1.4240180
C	6.2004810	3.7511490	-1.2886800
H	5.4169050	3.1968130	-1.8159190
H	7.1411640	3.5444890	-1.8136190
C	0.4826450	-5.8859760	1.2153200
H	0.3333190	-4.8746720	1.6069060

H	-0.1046350	-6.5603900	1.8488430
C	1.9668990	-6.2480790	1.3035140
H	2.2503610	-6.2515200	2.3613700
H	2.1185270	-7.2757710	0.9483830
C	2.8870580	-5.2951610	0.5389690
H	2.6788610	-4.2497810	0.7862850
H	3.9356990	-5.5007020	0.7714030
H	2.7735180	-5.3978020	-0.5440700
C	5.8940870	5.2457830	-1.3338910
H	6.6676620	5.7951650	-0.7819720
H	4.9498310	5.4340450	-0.8094290
C	5.8023040	5.7848580	-2.7577740
H	5.0123780	5.2767010	-3.3186380
H	5.5804670	6.8551930	-2.7653190
H	6.7419370	5.6352200	-3.2987990
C	-2.5748580	7.2822400	0.8361330
H	-3.4026250	7.3901480	1.5454120
H	-1.8510540	6.6083210	1.3073680
C	-1.9306160	8.6473190	0.5866140

H	-2.6574000	9.3090960	0.0981410
H	-1.7097370	9.1068500	1.5556670
C	-0.6488460	8.5924850	-0.2428280
H	0.0907930	7.9328020	0.2216050
H	-0.8285430	8.2251110	-1.2571730
H	-0.1982680	9.5842460	-0.3335610

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