Supplementary Information (SI) for Journal of Materials Chemistry C.

Supplementary Information

Investigating the Angle-Dependent Emission of Dye-Doped 3D Luminescent Opals: Optical Property Insights

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S1. Experimental

S1.1 Synthesis of 4-(dimethylamino)-2'-hydroxychalcone (2'OH4NDMe-chalcone)

In a round bottom flask 1.12 g (20 mmol, 1 eq.) of sodium hydroxide was dissolved in a mixture of methanol (20 mL) and deionized water (1 mL). Next, 2.40 mL of 2'-hydroxyacetophenone was added. The reaction mixture was stirred for 45 min, then 2.98 g (20 mmol, 1 eq.) of 4-(dimethylamino)benzaldehyde was added. The reaction was continued on a magnetic stirrer at room temperature until complete conversion of the substrates. After that, the reaction mixture was poured into water with ice to obtain a red precipitate. The crude product was recrystallized from 96% ethanol to obtain pure product as red, shiny crystals (717 mg, 2.68 mmol, 13.4% yield). The spectroscopic data of the synthesized compound are described below.

^{1}H NMR (600 MHz, $CDCl_3$) δ 13.17 (s, 1H), 7.94 – 7.89 (m, 2H), 7.60 – 7.56 (m, 2H), 7.48 – 7.43 (m, 2H), 7.01 (dd, J = 8.4, 1.2 Hz, 1H), 6.92 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 6.73 (d, J = 8.5 Hz, 2H), 3.06 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.65, 163.65, 152.29, 146.56, 135.81, 130.97, 129.51, 122.89, 120.55, 118.71, 118.64, 114.71, 112.22, 40.40.

HR ESI-MS (+) calculated product $C_{17}H_{18}NO_2$ – *m/z:* $[M + H]^+$ 268.1332, found $[M + H]^+$ 268.1338.

The ^{1}H NMR and ^{13}C NMR spectra are presented in Supplementary Data – Fig. S1 and Fig. S2.

S1.2 Synthesis of 1,4-diketo-2,5-diethyl-3,6-diphenylpyrrolo-[3,4-c]-pyrrole (DPP)

In a round bottom flask 0.5 g (1.73 mmol, 1 eq.) of Pigment Red 255 (3,6-diphenyl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-(2*H*,5*H*)-dione) and 1.2 g of potassium carbonate (8.65 mmol, 5 eq.) were suspended in 5 mL of *N,N*-dimethylformamide. The reaction mixture was stirred and heated (75 °C) for 6h, then 0.644 mL (8.65 mmol, 5 eq.) of bromoethane was added. The reaction was continued overnight on a magnetic stirrer at 75 °C. After that, the reaction mixture was poured into water with ice to obtain the orange precipitate. The crude product was purified using liquid column chromatography to obtain pure product as orange powder (550 mg, 1.59 mmol, 91.9% yield). The spectroscopic data of the synthesized compound are described below.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.9, 1.7 Hz, 2H), 7.57 – 7.49 (m, 3H), 3.81 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.77, 148.51, 131.30, 129.07, 128.85, 128.32, 110.01, 77.41, 37.07, 15.07.

HR ESI-MS (+) calculated product $C_{22}H_{21}N_2O_2$ – *m/z:* $[M + H]^+$ 345.1598, found $[M + H]^+$ 345.1614.

The ^{1}H NMR and ^{13}C NMR spectra are presented in Supplementary Data – Fig. S3 and Fig. S4.

S1.2 Synthesis of undoped and dye-doped PMMA spheres and preparation of 3D opals

All syntheses were carried out under a nitrogen atmosphere. Deionized water (160 mL) and a different amount of a monomer – MMA (10 – 40 mL) were placed in a three-necked round- bottom flask equipped with an overhead stirrer R50 (Cat), a reflux condenser and a thermometer. When the mixture temperature was stabilized at 70 or 80°C, a polymerization reaction initiator – 2,2'-azobis(2-methylpropionamidine) dihydrochloride (0.3 g) was added. Then, the mixture was stirred for 2 hours at the set temperature. Next, it was taken out from the heating bath and stirred for another 1 hour and finally, the content of the flask was stirred for 15 minutes under the air atmosphere. The colloidal polymer dispersion was filtered by gravity using a fast quality filter.

In order to purify the obtained dispersions from residual monomer, they were centrifuged three times and washed with the deionized water and re-dispersed using an ultrasonic bath. After the synthesis, the water dispersions of the purified spheres were used for fabrication of 3D colloidal crystals by gravitational sedimentation. The dispersions were left at the laboratory conditions for a time of several days in polystyrene or glass Petri dishes or crystallizers for evaporation of the dispersant. The parameters of the syntheses are presented in Table 1.

We prepared analogously a series of spheres and colloidal crystals doped with chosen luminescent dyes. During the syntheses, the selected dyes were first dissolved in MMA at around 0.5 wt% with respect to the monomer. Due to the lower solubility of POPOP in MMA, it was introduced into the flask as a solid along with water and MMA). This may have resulted in the actual dye concentration in PMMA nanoparticles to be lower than expected. However, this has not negatively affected the quality of the samples obtained. After typical purification procedure there were no crystals of the dye visible in the SEM images. The parameters of dye-doped spheres syntheses are also presented in the Table S1.

S2. Methods

S2.1 Characterization of photoluminescence properties - absorption and photoluminescence spectra of the dyes and dye-doped spheres

In the first step, a series of solutions of the studied dyes in ethyl acetate was prepared. The measurements of UV-Vis absorption spectra of the dye solutions were recorded on the Evolution 300 (Thermo Fisher) spectrophotometer. Then, measurements of the emission and the excitation spectra of the dye solutions and dye-doped spheres were carried on the FLS980 spectrofluorimeter equipped with a xenon lamp Xe1 (Edinburgh Instruments). The measurements were performed in quartz cuvettes. For the excitation of the dye solution the light at respective wavelength (λ_{exc}) was used: 360 nm – for POPOP, 400 nm – for coumarin 6 and DPP, and 420 nm – for DCM dye samples. For the excitation of the dye-doped spheres: 360 nm – for POPOP, 380 nm – for coumarin 6 and DCM, 400 nm – for DPP.

S2.2 Absolute Photoluminescence Quantum Yield measurements

QY of the dye-doped spheres and the studied dyes in the solid state were measured in the Integrating Sphere Assembly F-M01 (Edinburgh Instruments) dedicated to the FLS980 spectrofluorimeter. The producer of the equipment specified estimated uncertainty of the absolute QY determination at the level of 5% and repeatability uncertainty at the level of 3% for the standard measurement procedure. Independently, uncertainty of the QY results which is resulting from a different form of the sample and reference was determined by measurements of scattering of the light on the sample in the measurement setup, at a selected non-absorbing wavelength equal 700 nm. Maximum uncertainty was 4% in the absolute QY value.

For the QY measurements the dye-doped PMMA spheres were ground in a mortar. Two series of the samples were prepared. First – the dye-doped opal itself and second – the dye-doped opal mixed with $BaSO_4$ at proper weight concentration. For the second type, the weight fraction of the dye-doped PMMA spheres with respect to the $BaSO_4$ matrix was set at the level of: 35% – for POPOP, 5% – for coumarin 6 and DPP, 2% – for DCM, and 10% – for 2'OH4NDMe-chalcone doped spheres, respectively. QY of the selected dyes in the solid state was also determined in the same manner. The dyes (without the PMMA matrix) were ground in the mortar in two series, first – without and second – mixed with $BaSO_4$. The weight concentration of the dyes with respect to $BaSO_4$ was set at the levels similar to those in the opal samples. The ground materials were used for a preparation of pastilles using a hydraulic press – Mini-Pellet Press (Specac). For the QY measurements the samples in the form of the tablets were placed in the cup-shaped holder designed for the solid state samples. A reference sample was a pastille made of $BaSO_4$.

S2.3 The photoluminescence decay time measurements

Measurements of the decay time were performed on FLS980 (Edinburgh Instruments) spectrofluorometer, equipped with 360 nm and 450 nm laser diodes. Measurements were carried out for the dye-doped spheres, as well as for the selected dyes in solid state as well as their solutions in ethyl acetate.

S2.4 Measurements of angle-dependent emission color of the 3D opals

Measurements of the observed emission spectra depending on the detection angle of the fabricated 3D dye-doped PMMA opals were performed in a self-made setup, modified with respect to the setup for the Optical Bragg reflection measurements. CCD camera – QE65 Pro (Ocean Optics) equipped with optical fiber was used as a detector and it was mounted on the rotating arm. The sample was put on a glass substrate being on a height-adjustable stage, so that the top of the sample was adjusted to the axis of rotation of detector's arm. The light source of UV lamp VL-6.LC (Vilber Lourmat) with a short-pass filter cutting the spectrum below wavelength λ = 395 nm was used to excite the samples containing POPOP dye. Excitation of coumarin 6 and DCM samples was performed by nova Pro diode laser (RGB Lasersystems GmbH) emitting light of output power of 75 mW at λ = 405 nm. Gray filter was used to limit the light power from the laser. The 3D opal samples with a thickness not greater than 2 mm were excited from the bottom at the incident angle around 45°. For the measurement, the detector was collecting the emitted light from the top side of the sample at different angle. The detection angle with respect to the normal to the sample plane was set in a range from 0° to 60° and the emission spectrum was registered.

S3. Figures

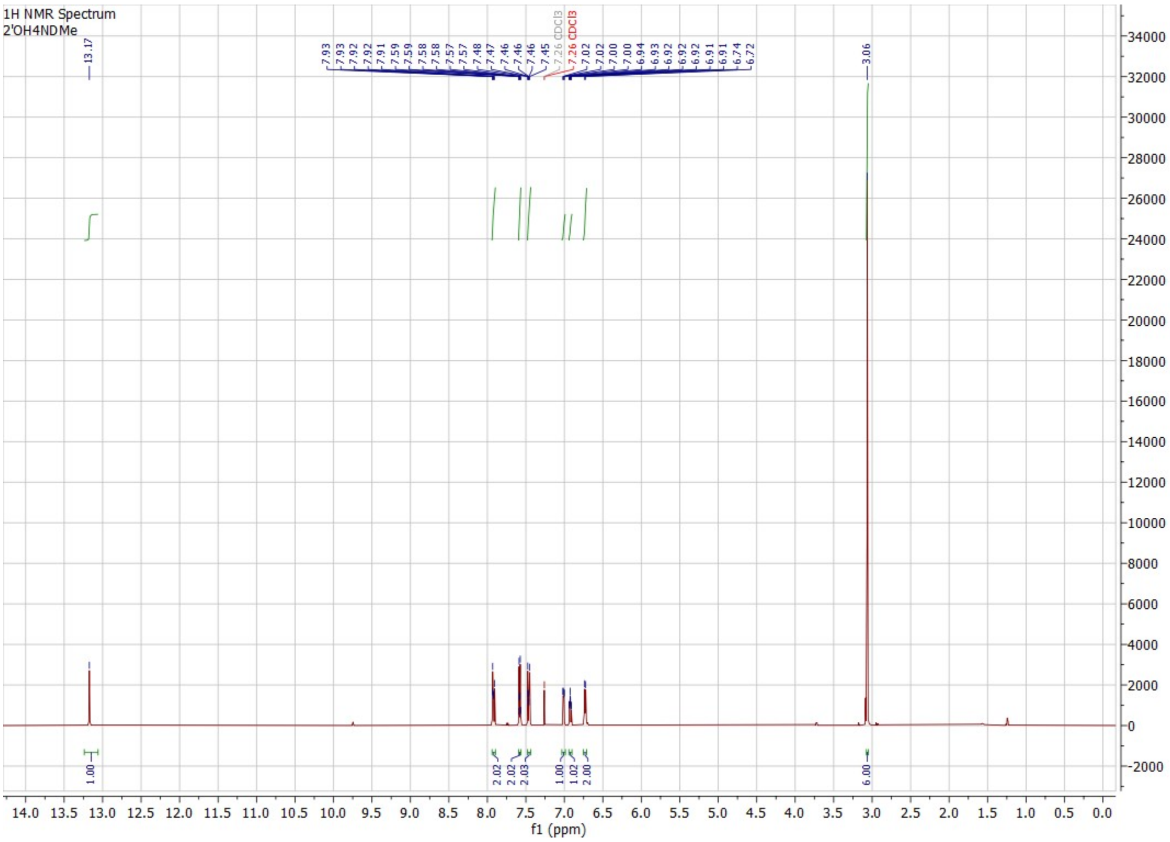


Figure S1. ^{1}H NMR spectrum of 2’OH4NDMe-chalcone.

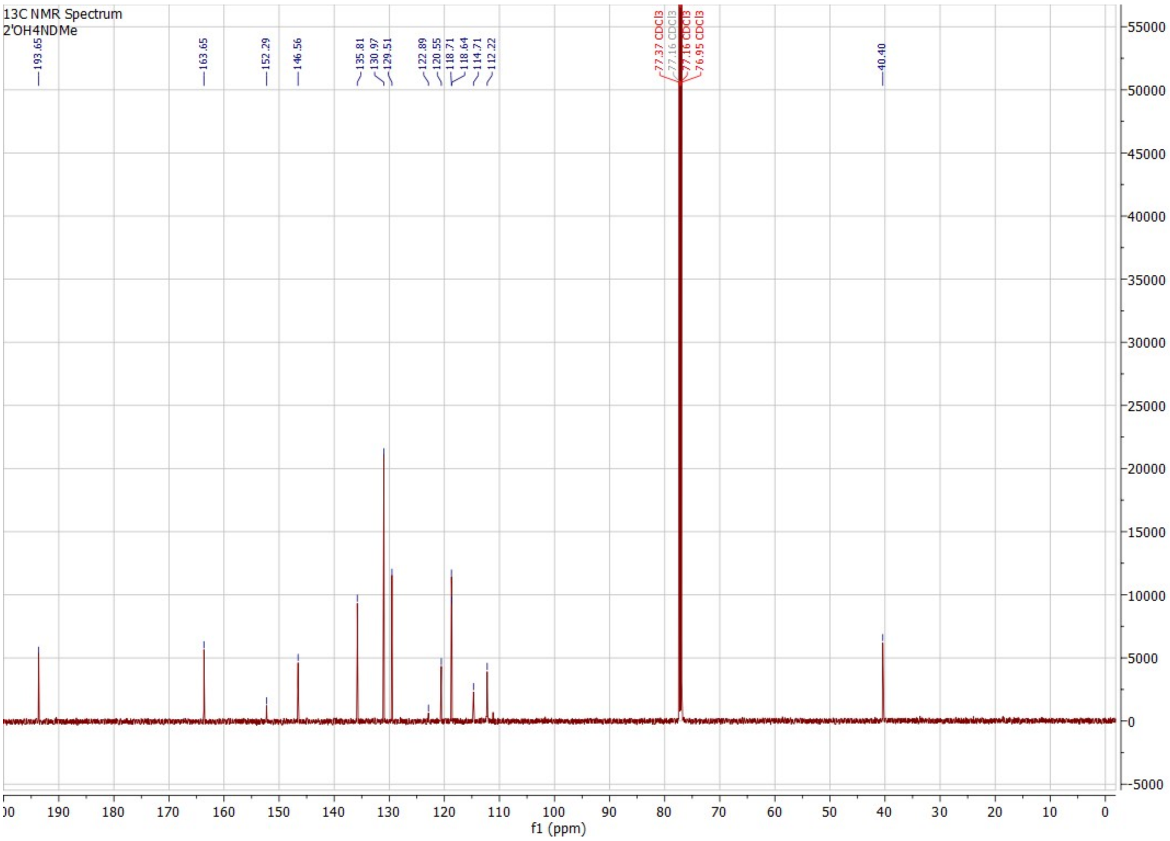


Figure S2. ^{13}C NMR spectrum of 2’OH4NDMe-chalcone.

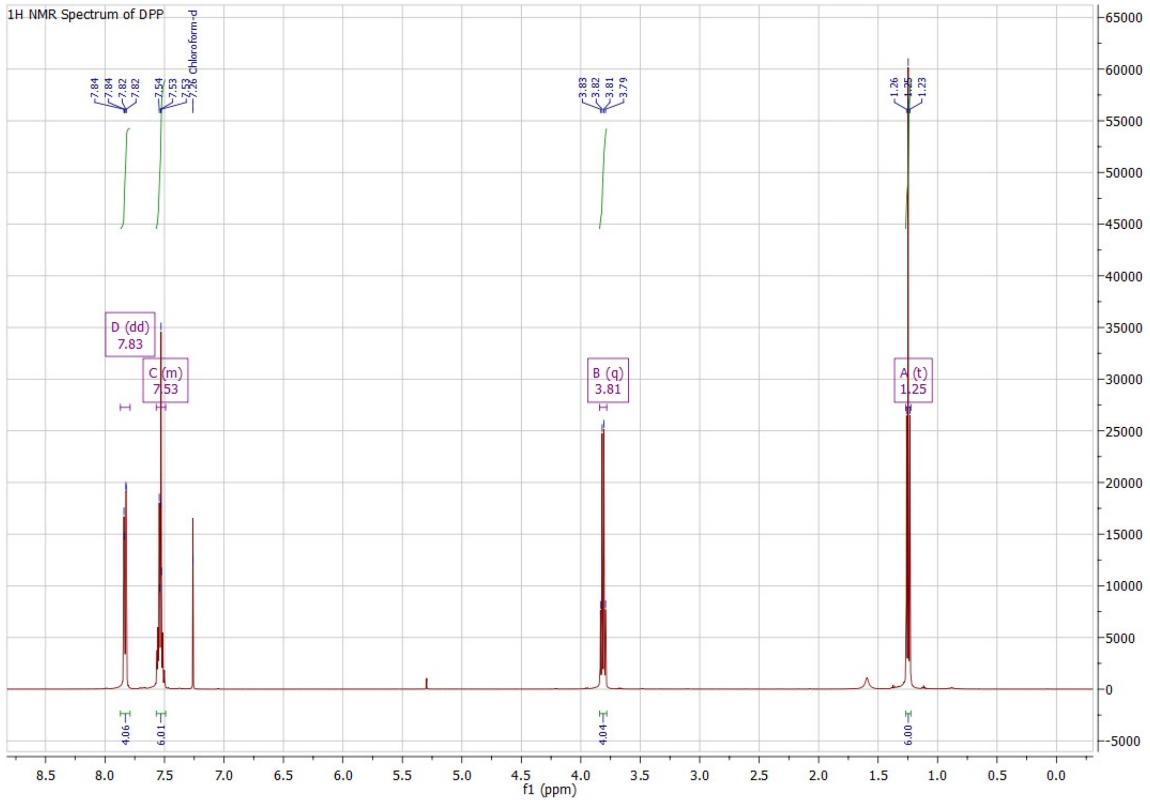


Figure S3. ^{1}H NMR spectrum of DPP.

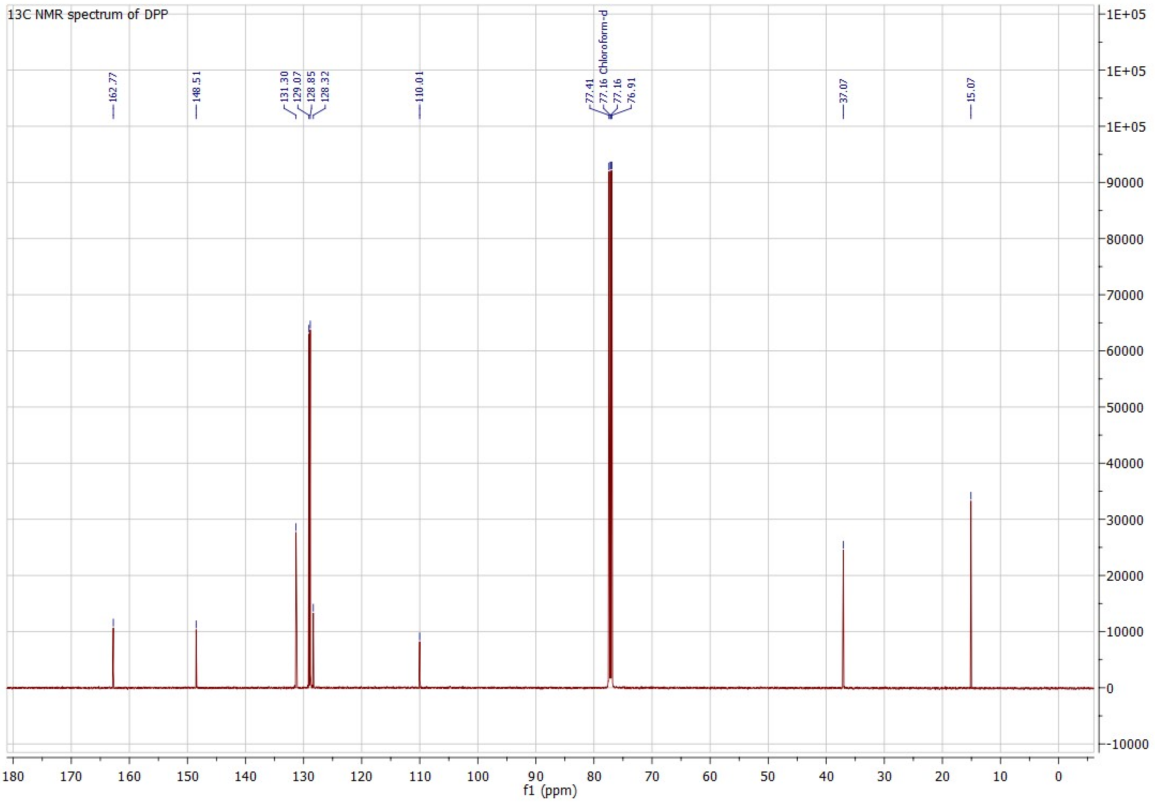
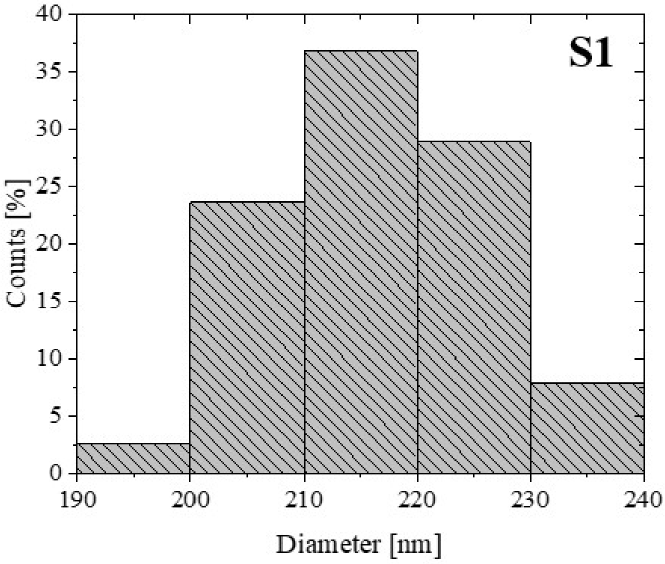


Figure S4. ^{13}C NMR spectrum of DPP.


S1
Counts [%]
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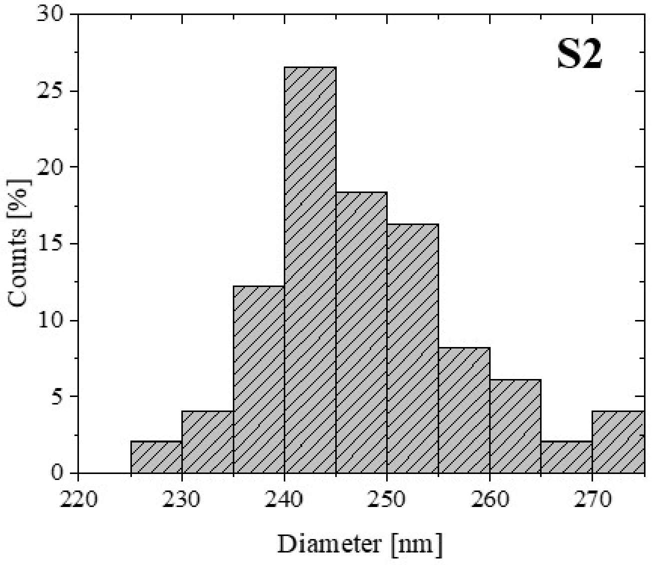
5
10
15
20
25
30
35
40
190
200
210
220
230
240
Diameter [nm]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Counts [%]
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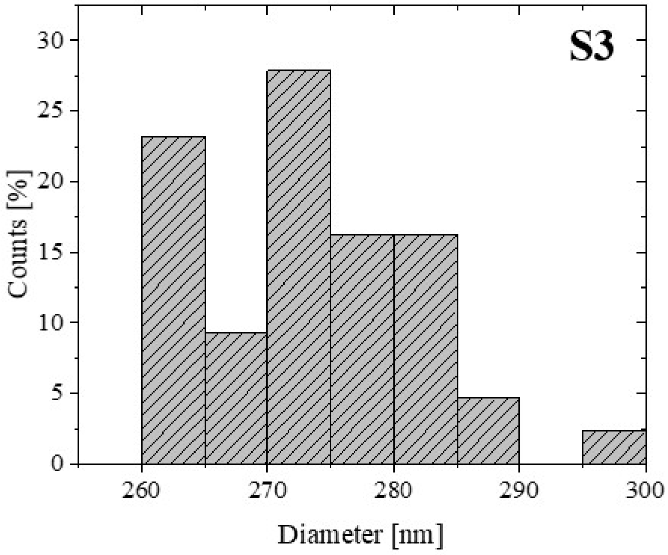
260
270
Diameter [nm]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280
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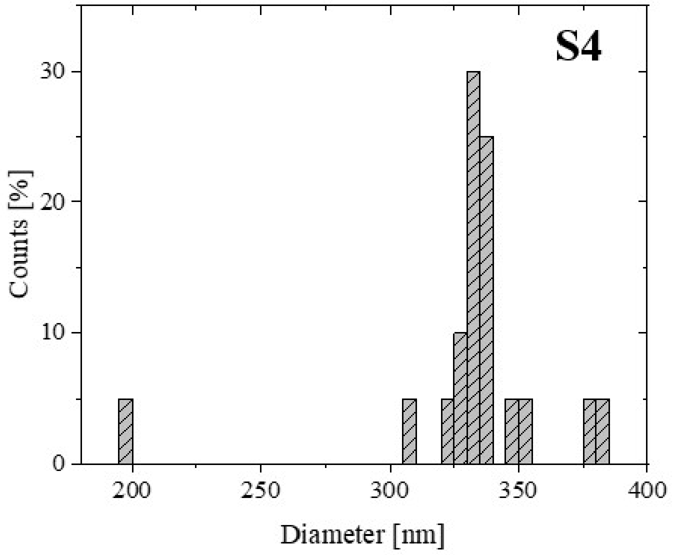
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350
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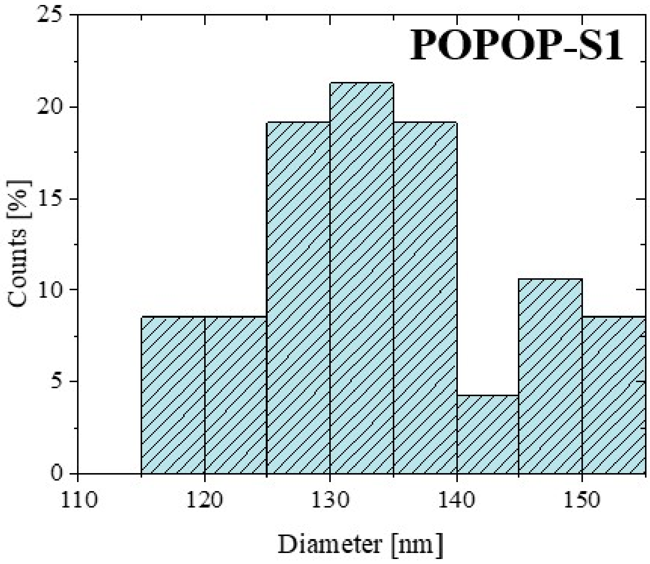
Diameter [nm]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Counts [%]
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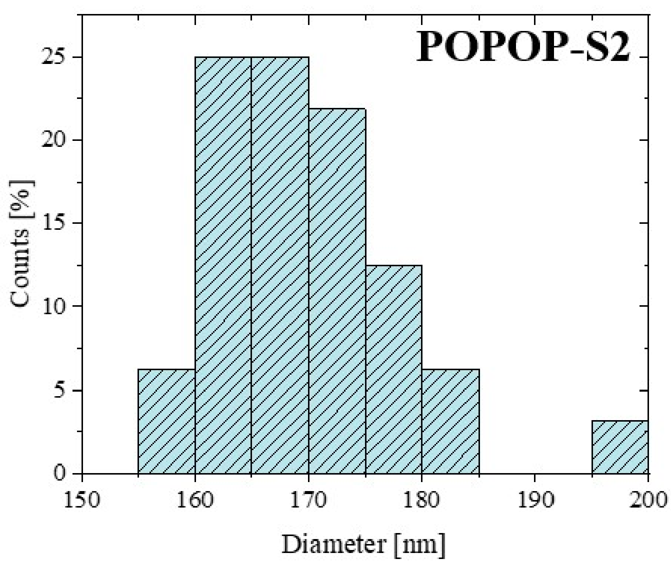
5
10
15
20
25
110
120
130
140
150
Diameter [nm]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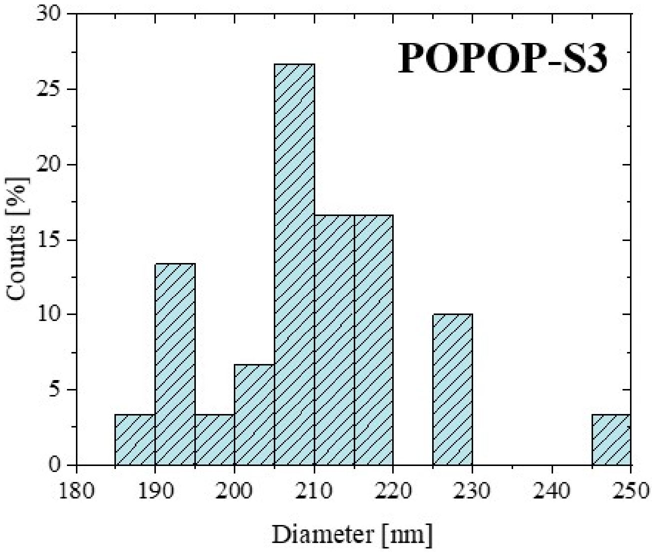
170
180
190
200
Diameter [nm]


POPOP-S3
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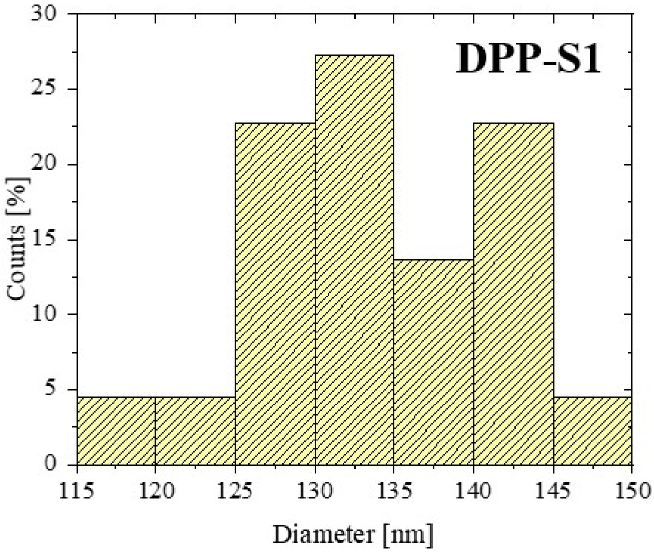
Diameter [nm]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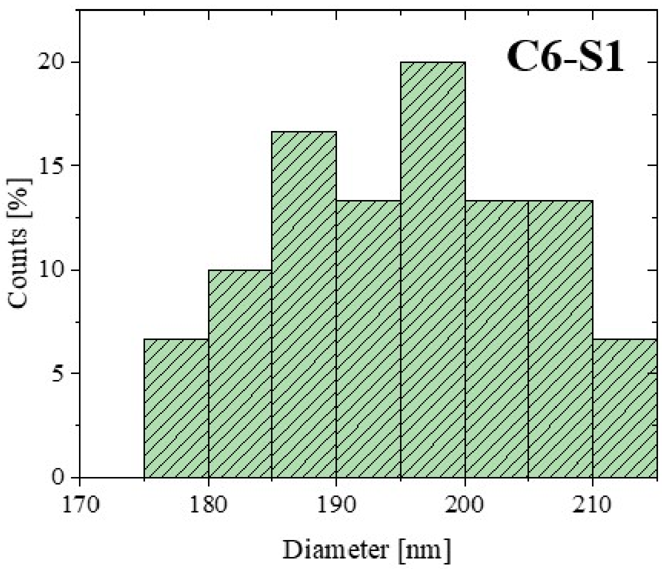
30
115
120
125
130
135
140
145
150
Diameter [nm]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Counts [%]
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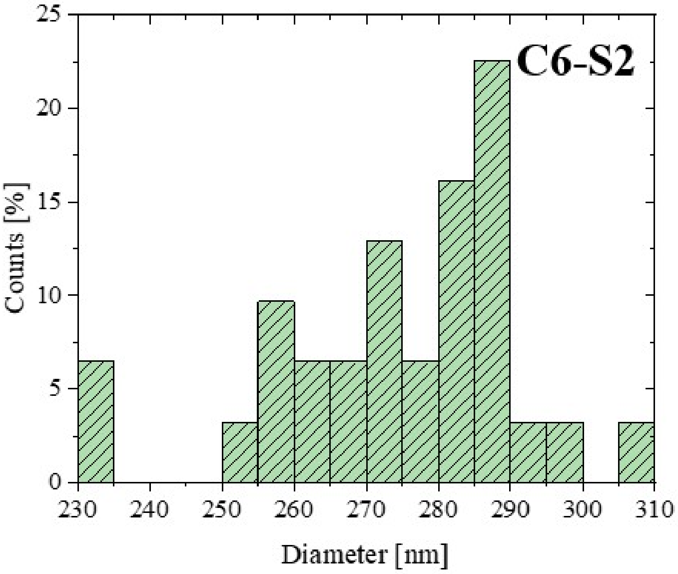
10
15
20
170
180
190
200
210
Diameter [nm]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240
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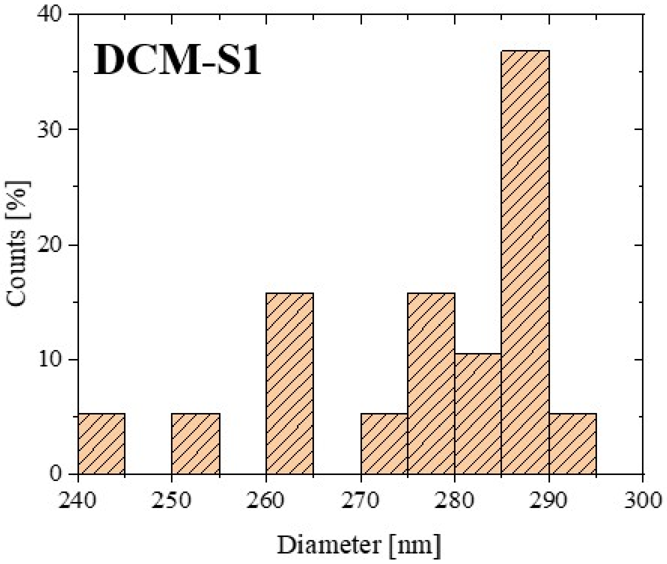
270
280
290
300
310
Diameter [nm]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Counts [%]
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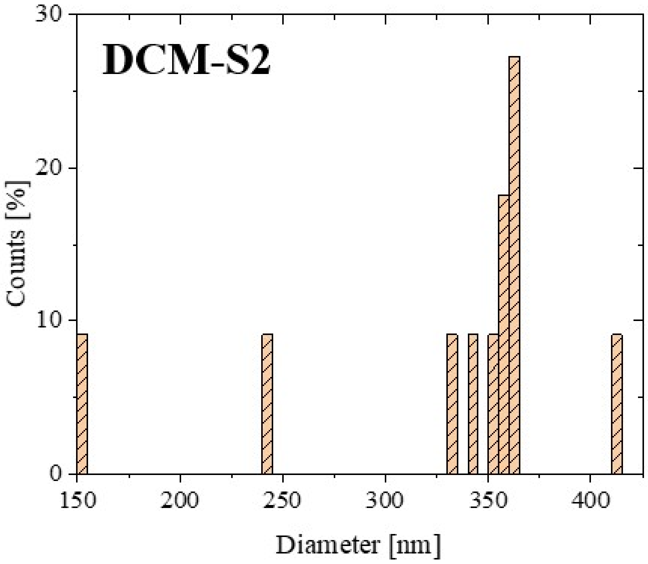
30
40
240
250
260
270
280
290
300
Diameter [nm]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Counts [%]
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20
30
150
200
250
300
350
400
Diameter [nm]

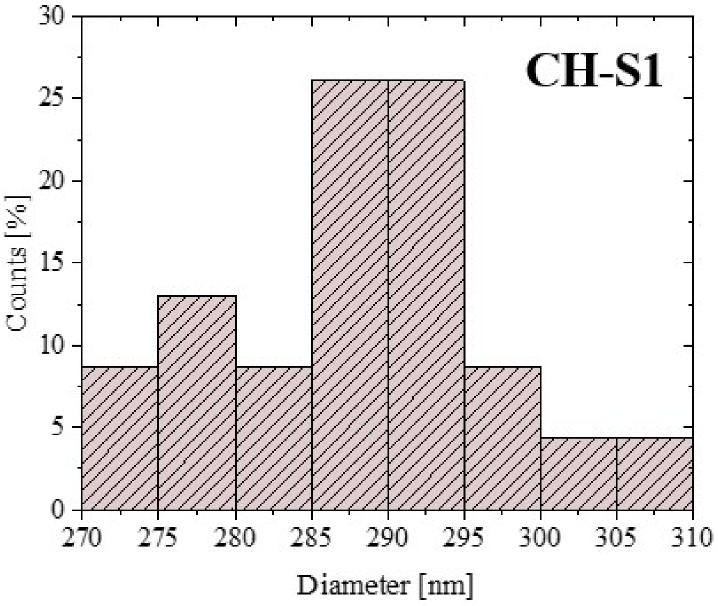

Figure S5. Histograms of the size distribution of the synthesized dye-doped PMMA spheres.

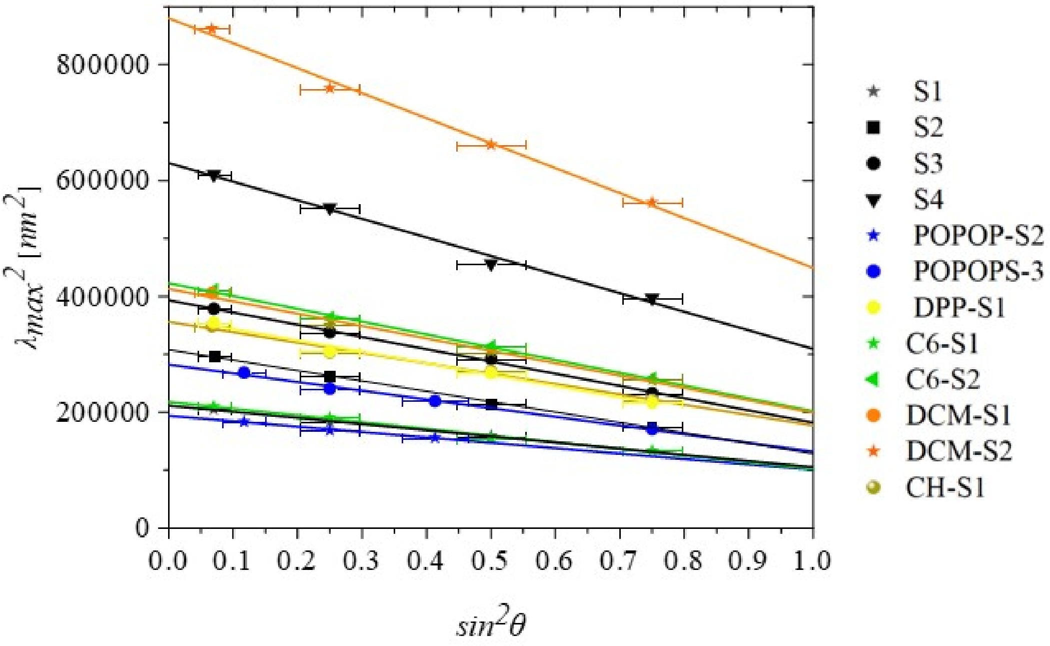

Figure S6. Plot of λ^2_{max} versus $\sin^2 \vartheta$, where λ_{max} is the position of the reflection band maximum and ϑ is the angle of incidence with respect to the normal to the (111) plane of the opal.

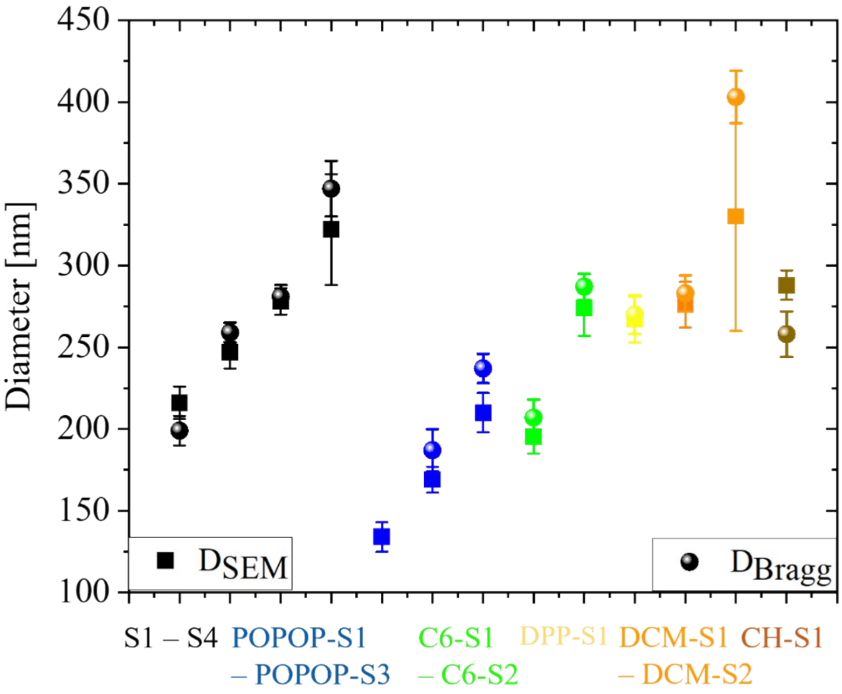

Figure S7. Comparison of the relationship between the size of the spheres obtained by the SEM and Bragg reflectance bands measurements.

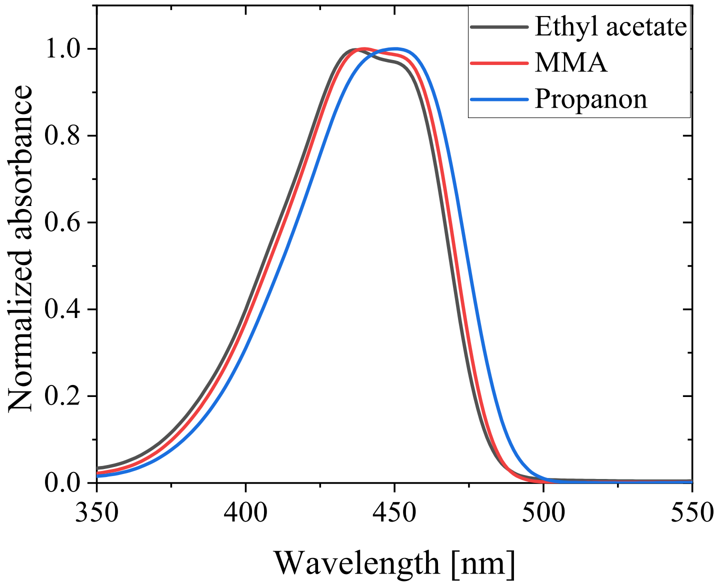

Figure S8. Absorption spectra of the coumarin 6 dye in different solvents.

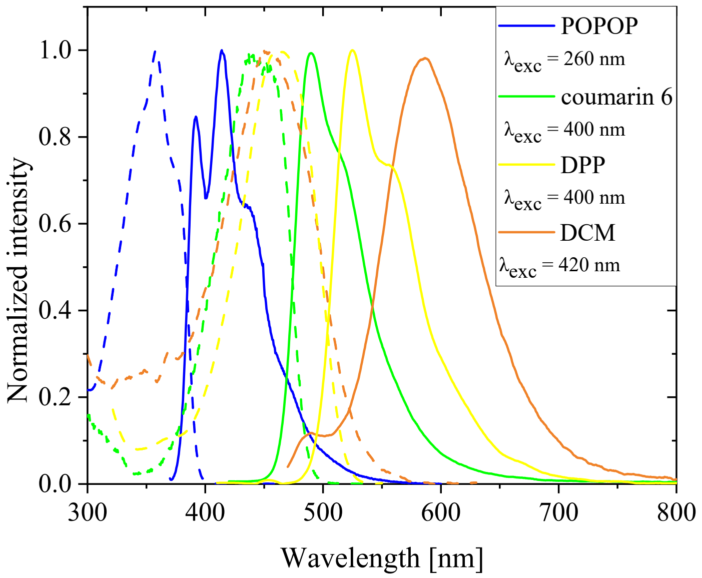

Figure S9. Normalized emission and excitation spectra of the studied dyes dissolved in ethyl acetate (dotted lines show the excitation spectra).

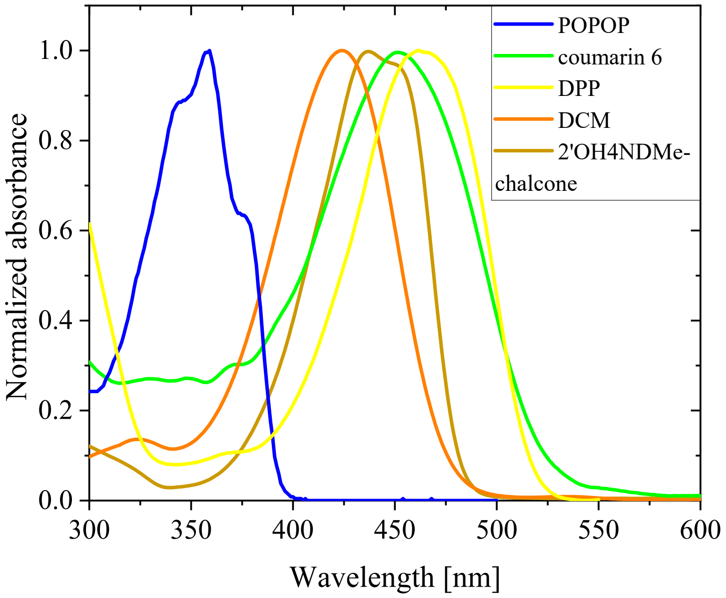

Figure S10. Absorption spectra of the ethyl acetate solutions of the dyes selected for the study.

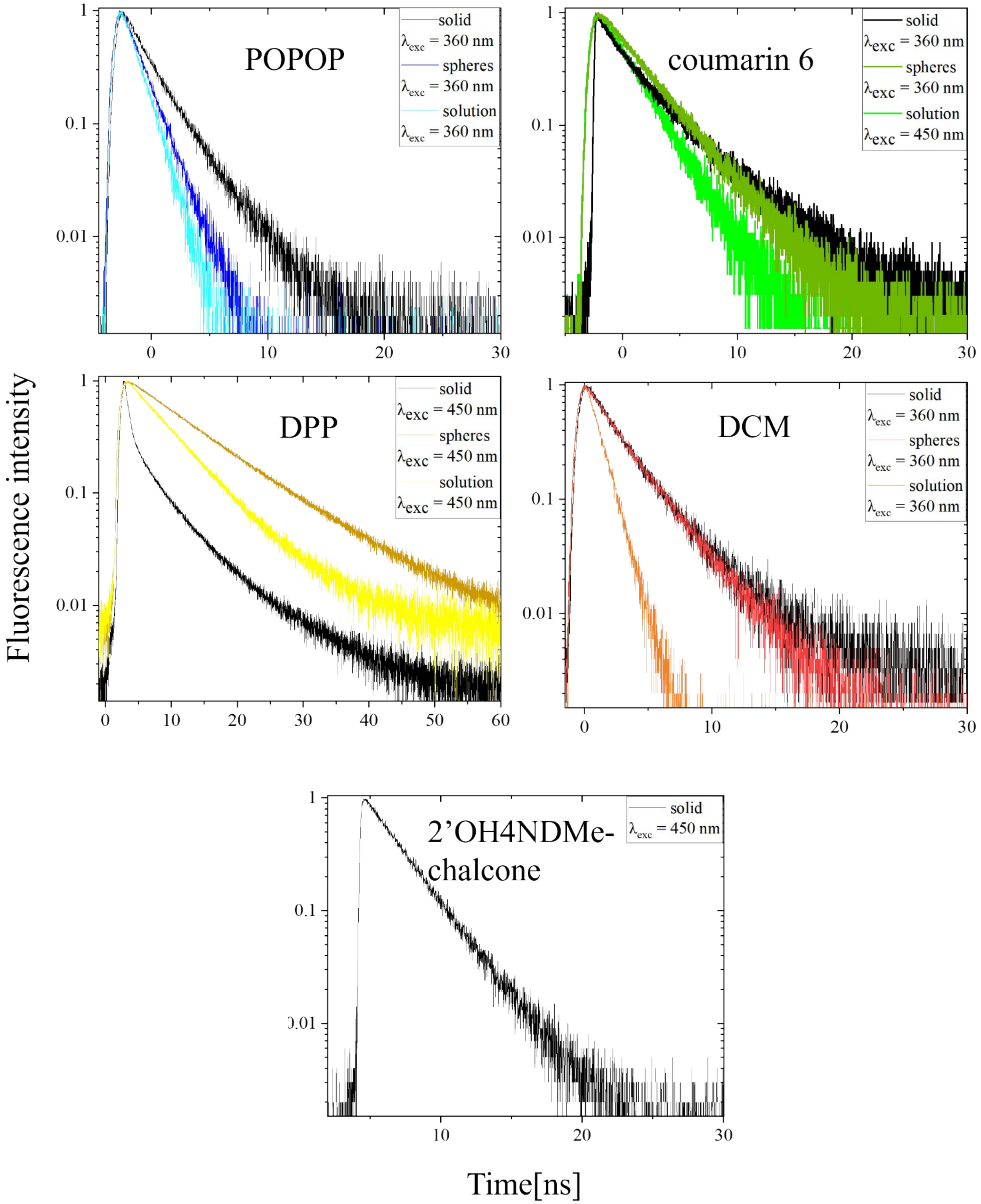

Figure S11. Luminescence decay time curves for the studied 3D dye-doped opals and dyes solutions.

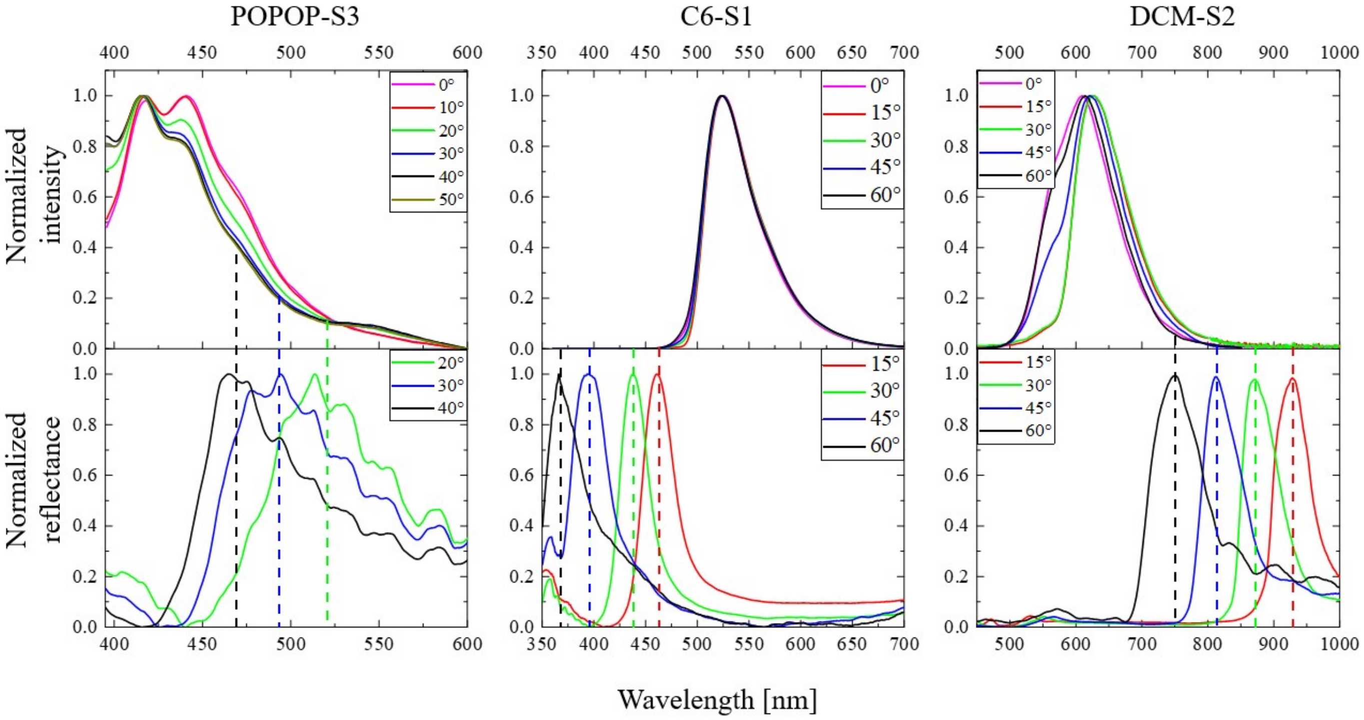

Figure S12. Normalized emission spectra (top) and normalized reflectance spectra (bottom) of the synthesized PMMA opals doped with dyes.

S4. Tables

Table S1. Parameters of the syntheses of the undoped and the dye-doped PMMA spheres.

sample	**temperature [°C]**	**H_2O volume [mL]**	**initiator mass[g]**	**MMA volume [mL]**	**dye mass [mg]**
S1	80	160	0.300	10	-
S2	80	160	0.300	15	-
S3	80	160	0.300	20	-
S4	70	160	0.300	40	-
POPOP-S1	80	160	0.300	10	50
POPOP-S2	80	160	0.300	12.5	62.5
POPOP-S3	80	160	0.300	16	80
C6-S1	80	160	0.300	10	50
C6-S2	80	160	0.300	15	75
DCC-S1	80	160	0.300	20	100
DCM-S1	80	160	0.300	20	100
DCM-S2	70	160	0.200	40	200
CH-S1	80	160	0.300	20	100

Table S2. Results of the spheres size determination by SEM microscopy and Bragg reflection band measurements.

sample	SEM measurement			reflection band measurement		
	$D_{SEM} \pm \sigma$ [nm]	PI	RSD [%]	$D_{Bragg} \pm \sigma$ [nm]	$n_{avg} \pm \sigma$	λ_{max} (θ = 0°)* [nm]
S1	**216 ± 10**	1.007	4.6	**199 ± 9**	1.42 ± 0.08	459
S2	**247 ± 10**	1.004	3.9	**259 ± 6**	1.31 ± 0.04	555
S3	**273 ± 8**	1.002	3.1	**281 ± 7**	1.37 ± 0.04	627
S4	**322 ± 34**	1.022	10.6	**347 ± 17**	1.40 ± 0.08	794
POPOP-S1	**134 ± 9**	1.013	7.2	not determined		
POPOP-S2	**169 ± 8**	1.010	4.9	**187 ±13**	1.44 ± 0.11	440
POPOP-S3	**210 ± 12**	1.011	6.0	**237 ± 9**	1.38 ± 0.06	531
C6-S1	**195 ± 10**	1.006	5.1	**207 ± 11**	1.37 ± 0.09	466
C6-S2	**274 ± 17**	1.012	6.2	**287 ± 8**	1.39 ± 0.04	650
DCC-S1	**267 ± 14**	1.007	5.5	**270 ± 12**	1.36 ± 0.08	602
DCM-S1	**276 ± 14**	1.008	5.1	**283 ± 11**	1.39 ± 0.07	643
DCM-S2	**330 ± 70**	1.084	21.7	**403 ± 16**	1.43 ± 0.07	938
CH-S1	**288 ± 9**	1.003	3.1	**258 ± 14**	1.39 ± 0.09	597

* λ_{max}(θ = 0°) is experimentally determined value of λ_{max} at normal incidence (θ = 0°)

Table S3. Zeta potential measurement results.

sample	**Zeta Potential [mV]**
S3	48.0 ± 0.9
POPOP-S3	49.5 ± 0.8
C6-S2	50.7 ± 1.5
DPP-S1	45.5 ± 1.0
DCM-S1	44.0 ± 0.9
CH-S1	46.2 ± 0.7

Table S4. Summary of the results of QY and photoluminescence decay time measurement for the studied dyes in various matrixes.

dye	**type of sample**	Φ_f	**τ [ns]**
POPOP	solution	75% (EtOH) [40] 76% (cyclohexane) [40]	1.2 (EA)
	solid	17% (λ_{exc} = 340 nm)	2.58
	PMMA spheres	12% (λ_{exc} = 340 nm)	1.58
coumarin 6	solution	89% (EtOH) [46] 60% (cyclohexane) [48] 57% (acetonitrile) [48]	2.5 (EA)
	solid	10% (λ_{exc} = 460 nm)	4.21
	PMMA spheres	92% (λ_{exc} = 430 nm)	3.38
DPP	solution	87% (EA)	6.60 (EA)
	solid	2% (λ_{exc} = 430 nm)	6.64
	PMMA spheres	86% (λ_{exc} = 430 nm)	10.48
DCM	solution	80% (DMSO) [49] 57% (1-propanol) [49]	1.1 (EA)
	solid	3% (λ_{exc} = 430 nm)	3.06
	PMMA spheres	34% (λ_{exc} = 430 nm)	2.96
2’OH4NDMe-chalcone	solution	0.5% (ACN) [38] 10% (THF) [38]	n/d
	solid	18.5% [37]	n/d
		13% (λ_{exc} = 400 nm)	2.52
	PMMA spheres	<1% (λ_{exc} = 400 nm)	n/d

Table S5. Full results of the QY measurements.

sample	matrix	QY [%]
POPOP	$BaSO_4$	8
	–	17
POPOP-S2	PMMA spheres, $BaSO_4$	16
	PMMA spheres	12
coumarin 6	$BaSO_4$	5
	–	10
C6-S2	PMMA spheres, $BaSO_4$	74
	PMMA spheres	92
DPP	$BaSO_4$	4
	–	2
DPP-S1	PMMA spheres, $BaSO_4$ (1:10)	94
	PMMA spheres, $BaSO_4$ (2:10)	85
	PMMA spheres	86
DCM	$BaSO_4$	7%
	–	3%
DCM-S1	PMMA spheres, $BaSO_4$	42%
	PMMA spheres	34%
2’OH4NDMe-chalcone	$BaSO_4$	1%
	–	13%
	KBr*	13%
CH-S1	PMMA spheres, $BaSO_4$	<1%
	PMMA spheres	<1%

* for the measurement in KBr matrix the sample was prepared in the same manner, but KBr pastille was used a reference sample