

Water-soluble/visible-light-sensitive naphthalimide derivative-based photoinitiating systems: 3D printing of antibacterial hydrogels

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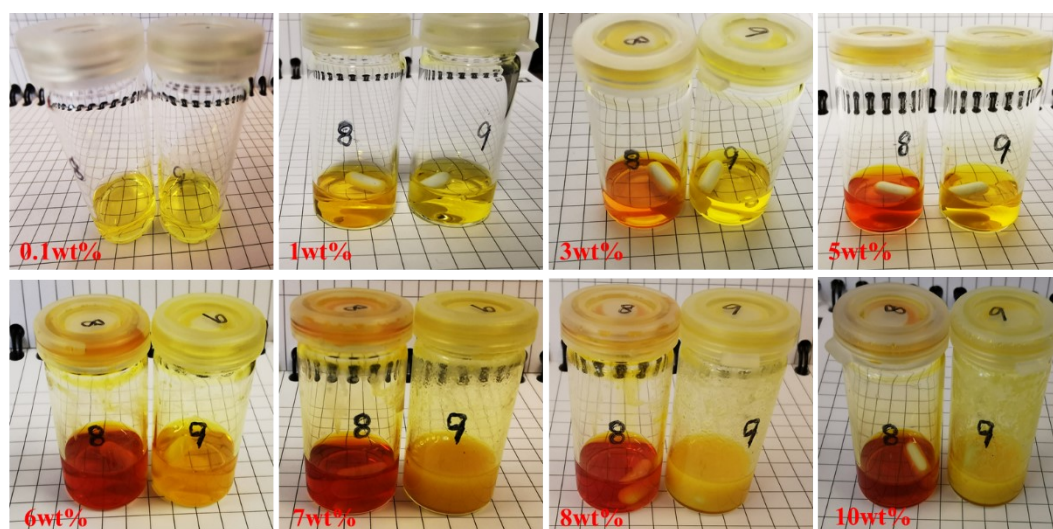


Figure S1. Pictures of dyes 8 and 9 in water with different concentrations of 0.1 wt%, 1 wt%, 0.1 wt%, 3 wt%, 5 wt%, 6 wt%, 7 wt%, 8 wt% and 10 wt%.

DYEs	λ_{\max} (nm)	ϵ_{\max} ($M^{-1} cm^{-1}$)	$\epsilon_{@405nm}$ ($M^{-1} cm^{-1}$)
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8	300	25 260	4280
9	325	18 530	9150
	400	9230	

Table S1. Summary of light absorption properties of dyes 8 and 9 in water: maximum absorption wavelengths (λ_{\max}); molar extinction coefficients at λ_{\max} (ϵ_{\max}) and the emission wavelength of the LED@405 nm ($\epsilon@405\text{nm}$).

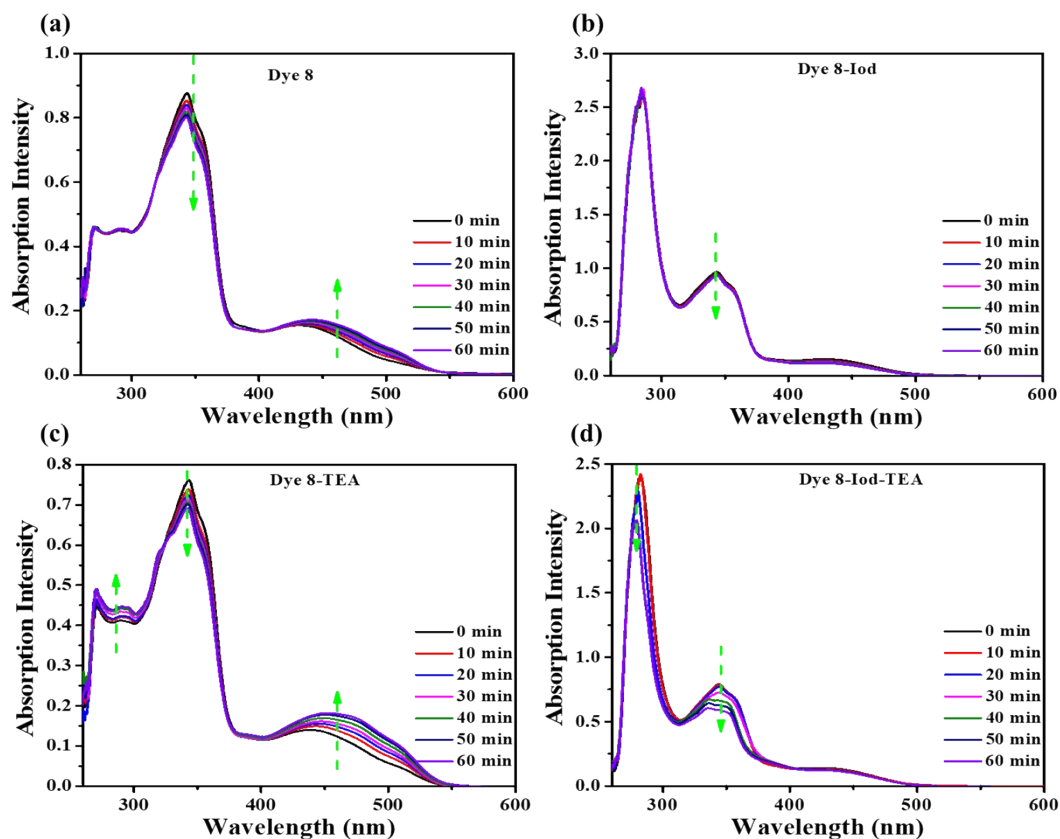


Figure S2. The photolysis of dyes 8 based one/two/three-component systems (a) dye 8, (b) dye 8-Iod, (c) dye 8-TEA, (d) dye 8-Iod-TEA) in DMSO under LED@405nm.

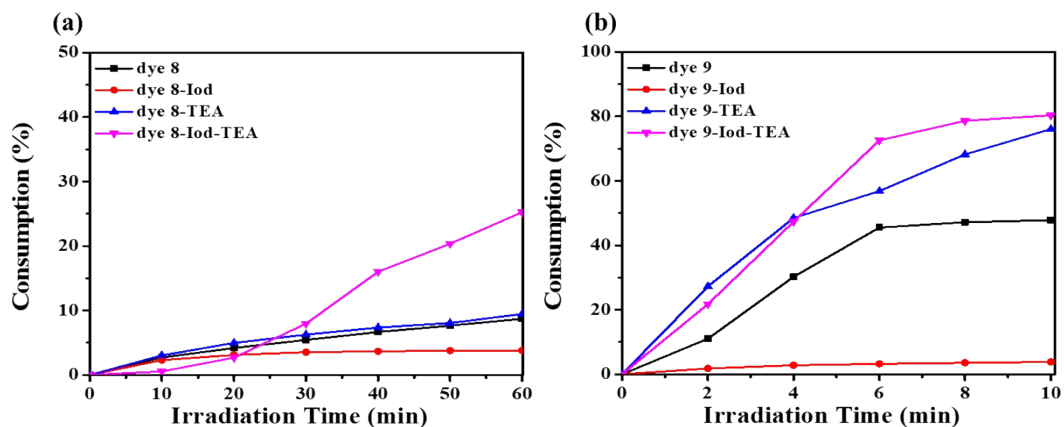


Figure S3. The consumption of (a) dyes 8 and (b) dye 9 during the photolysis process.

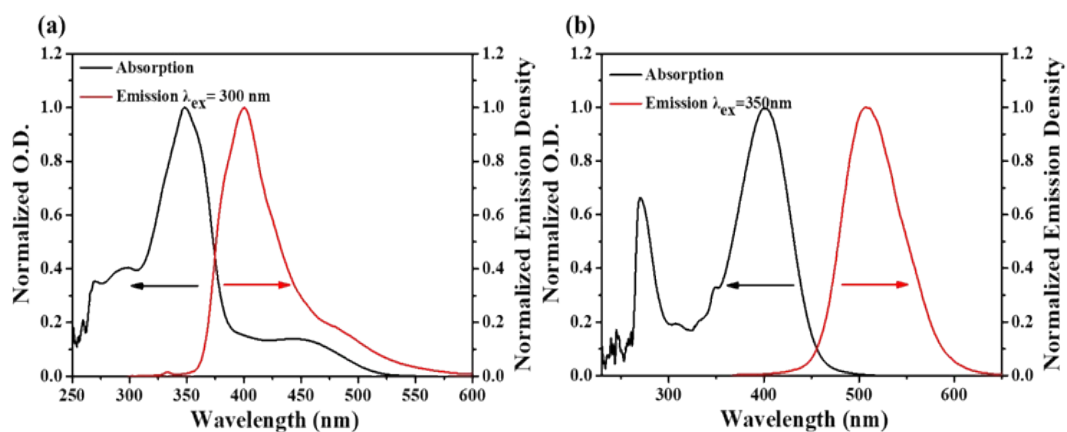


Figure S4. Singlet state energy of (a) dye 8 and (b) dye 9 determined in water.

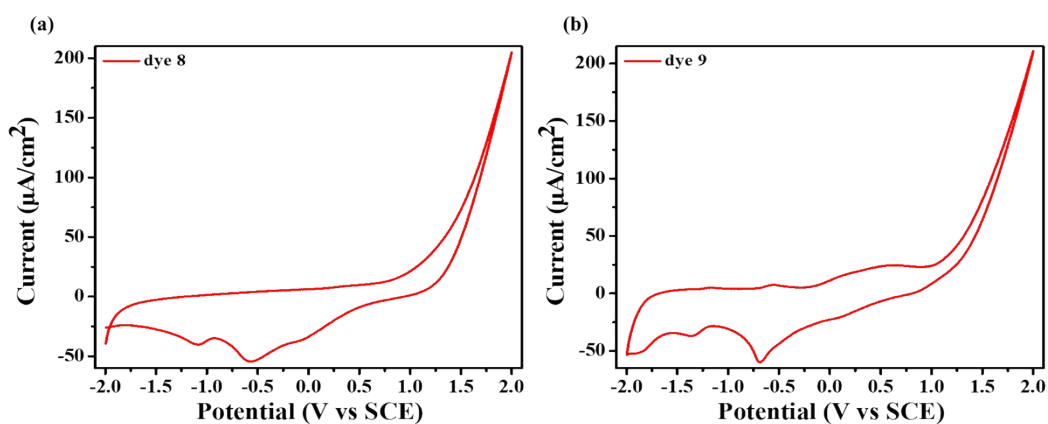


Figure S5. Cyclic voltammetry of (a) dye 8 and (b) dye 9 determined in DMSO.

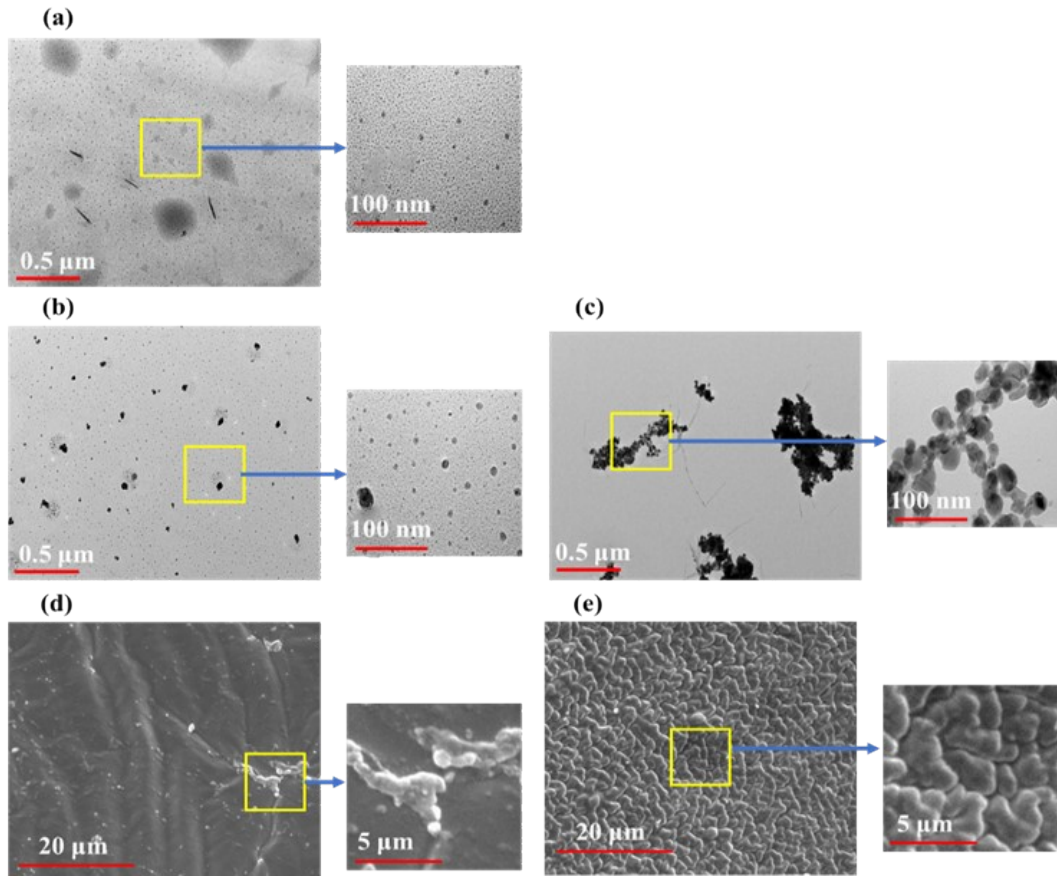


Figure S6. TEM images of (a) AgNPs prepared in DMF solution after irradiation for 100 min; (b) AgNPs prepared in water before open the light; (c) AgNPs prepared in water after irradiation for 30 min; (d) AgNPs on the down surface of obtained PEG-hydrogels from RT-FTIR experiment; (e) AgNPs on the upper surface of obtained PEG-hydrogels from RT-FTIR experiment.

	Dye 8	Dye 9	Dye 8-AgNO₃	Dye 9-AgNO₃	
Route 1	Original volume (V_0 , mm ³)	28.86	30.06	14.70	16.88
	Volume at Swelling Equilibrium (V_1 , mm ³)	41.69	55.55	19.86	23.91
	Volume after Dehydration (V_2 , mm ³)	18.80	17.22	8.98	8.51
	R (%)	144	185	135	141
	Original volume (V_0 , mm ³)	26.52	31.50	15.75	17.15
Route 2	Volume after Dehydration (V_1' , mm ³)	21.45	18.34	10.85	10.66
	Volume at Swelling Equilibrium (V_2' , mm ³)	43.22	53.86	23.81	21.43
	R (%)	163	173	151	125

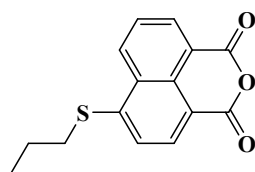
Table S2. Volumes of the obtained 3D patterns during two swelling routes: initial volume (V_0), volumes at swelling equilibrium (V_1/V_2'), volume after dehydration (V_3/V_1') as well as the volume change ratio (R/R').

Synthesis of photoinitiators

General informations

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^1H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^1H (400 MHz) and ^{13}C (100 MHz). The ^1H chemical shifts were referenced to the solvent peak CDCl_3 (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak CDCl_3 (77.0 ppm). All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis.

Synthesis of 6-(propylthio)-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (dye 1)



Chemical Formula: C₁₅H₁₂O₃S

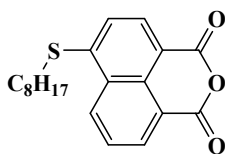
Molecular Weight: 272.3180

To a stirred solution of 6-bromobenzo[*de*]isochromene-1,3-dione (1.60 g, 5.77 mmol, M = 277.07 g/mol) and potassium carbonate (0.51 g) in DMF (15 mL) was added propanethiol (0.56 mL, 0.46 g, 5.99 mmol, M = 76.16 g/mol, d = 0.820). The mixture was heated at 50°C overnight. After cooling, the suspension was poured into 40 mL of distilled water, the precipitate was collected by filtration, washed with distilled water, ether, pentane and dried under vacuum (1.38 g, 88% yield). Analyses were consistent with those previously reported in the literature [I. Ott, Y. Xu, J. Liu, M. Kokoschka, M. Harlos, W. S. Sheldrick, X. Qian, *Bioorg. Med. Chem.* 16 (2008) 7107–7116].

¹H NMR (400 MHz, CDCl₃) δ 8.62 (d, *J* = 7.9 Hz, 2H), 8.46 (d, *J* = 7.9 Hz, 1H), 7.78 (t, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 3.18 (t, *J* = 7.3 Hz, 2H), 1.96 – 1.80 (m, 2H), 1.15 (t, *J* = 7.4 Hz, 3H)

HRMS (ESI MS) *m/z*: theor: 272.0508 found: 272.0509 (M⁺ detected)

Synthesis of 6-(octylthio)benzo[*de*]isochromene-1,3-dione (dye 2)



Chemical Formula: C₂₀H₂₂O₃S

Molecular Weight: 342.4530

To a stirred solution of 6-bromobenzo[*de*]isochromene-1,3-dione (1.60 g, 5.77 mmol, M = 277.07 g/mol) and potassium carbonate (0.51 g) in DMF (15 mL) was added 1-octanethiol (1.0 mL, 0.88 g, 5.99 mmol, M = 146.29 g/mol, d = 0.843). The mixture was heated at 50°C overnight. After cooling, the suspension was poured into 40 mL of distilled water. The precipitate was collected by filtration, washed with distilled water, and dried under vacuum

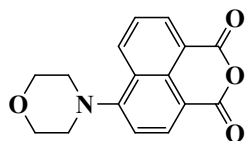
(1.46 g, 72% yield). Analyses were consistent with those previously reported in the literature [P. Xiao, F. Dumur, J. Zhang, B. Graff, F. Morlet-Savary, J.-P. Fouassier, D. Gigmes, J. Lalevée, J. Polym. Sci. A Polym. Chem. 53 (2015) 2860–2866]

^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, 3H, $J = 6.2$ Hz), 1.20-1.40 (m, 8H), 1.52-1.54 (m, 2H), 1.82-1.84 (m, 2H), 3.19 (t, 2H, $J = 7.1$ Hz), 7.55 (d, 1H, $J = 7.7$ Hz), 7.79 (t, 1H, $J = 7.7$ Hz), 8.47 (d, 1H, $J = 7.6$ Hz), 8.63 (d, 2H, $J = 7.7$ Hz)

^{13}C NMR (101 MHz, CDCl_3) δ 14.1, 22.6, 28.1, 29.0, 29.08, 29.10, 31.7, 32.7, 114.3, 119.3, 122.3, 126.9, 129.5, 130.4, 131.4, 132.9, 133.6

HRMS (ESI MS) m/z : theor: 342.1290 found: 342.1292 (M^+ detected)

Synthesis of 6-morpholino-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (dye 3)



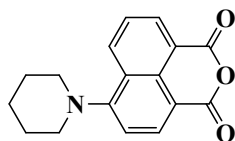
Chemical Formula: $\text{C}_{16}\text{H}_{13}\text{NO}_4$
Molecular Weight: 283.2830

4-Bromo-1,8-naphthalic anhydride (2.77 g, 10 mmol) and morpholine (5 mL) were dissolved in 2-ethoxyethanol and the solution was refluxed overnight. The resulting solution was cooled to room temperature and water was added. The precipitate was collected by filtration, washed with distilled water, and dried under vacuum (1.76 g, 62% yield). Analyses were consistent with those previously reported in the literature [C. Li, Y. Wang, S. Huang, X. Zhang, X. Kang, Y. Sun, Z. Hu, L Han, L. Du, Y. Liu, Talanta 188 (2018) 316–324]

^1H NMR (400 MHz, CDCl_3) δ 8.60 (dd, $J = 7.3, 1.2$ Hz, 1H), 8.55 (d, $J = 8.1$ Hz, 1H), 8.48 (dd, $J = 8.5, 1.2$ Hz, 1H), 7.75 (dd, $J = 8.5, 7.3$ Hz, 1H), 7.28 – 7.24 (m, 1H), 4.07 – 4.00 (m, 4H), 3.32 (dd, $J = 5.5, 3.8$ Hz, 4H)

HRMS (ESI MS) m/z : theor: 283.0845 found: 283.0849 (M^+ detected).

Synthesis of 6-(piperidin-1-yl)-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (dye 4)



Chemical Formula: C₁₇H₁₅NO₃

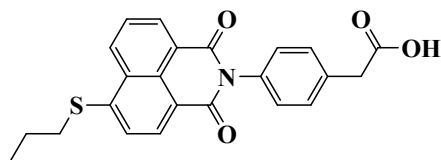
Molecular Weight: 281.3110

4-Bromo-1,8-naphthalic anhydride (2.77 g, 10 mmol) and piperidine (5 mL) were dissolved in 2-ethoxyethanol and the solution was refluxed overnight. The resulting solution was cooled to RT and water was added. The precipitate was collected by filtration, washed with distilled water, and dried under vacuum (2.42 g, 86% yield). Analyses were consistent with those previously reported in the literature [J.X. Ong, W.H. Ang, Chem Asian J.15 (2020) 1449–1455]

¹H NMR (400 MHz, CDCl₃) δ 8.57 (dd, *J* = 7.3, 1.2 Hz, 1H), 8.49 (d, *J* = 8.2 Hz, 1H), 8.45 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.71 (dd, *J* = 8.5, 7.3 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 3.34 – 3.26 (m, 4H), 1.96 – 1.85 (m, 4H), 1.76 (dd, *J* = 11.1, 5.6 Hz, 2H)

HRMS (ESI MS) *m/z*: theor: 281.1052 found: 281.1050 (M⁺ detected).

Synthesis of 2-(4-(1,3-dioxo-6-(propylthio)-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)phenyl)acetic acid (dye 5)



Chemical Formula: C₂₃H₁₉NO₄S

Molecular Weight: 405.4680

A mixture of 6-(propylthio)-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione (0.79 g, 2.92 mmol, M = 272.32 g/mol) and 4-aminophenylacetic acid (0.44 g, 2.92 mmol, M = 151.16 g/mol) were dissolved in DMF (50 mL) and the solution was refluxed overnight. After cooling, the solvent was removed under reduced pressure. The residue was purified by column chromatography

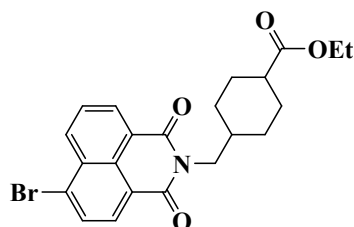
(SiO₂) using a mixture of eluent (DCM:THF). For higher purity, the product was dissolved in a minimum of ethanol and cooled in the fridge for one night. The yellow solid was filtered off, washed with cold ethanol and dried under vacuum (852 mg, 72% yield).

¹H NMR (400 MHz, DMSO-d₆) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 7.3 Hz, 1H), 8.39 (d, *J* = 7.9 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.39 (dd, *J* = 16.8, 8.3 Hz, 2H), 7.29 (dd, *J* = 14.8, 7.8 Hz, 2H), 3.68 (s, 2H), 3.28 (t, *J* = 7.2 Hz, 2H), 1.85 – 1.69 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H)

Anal. Calc. for C₂₃H₁₉NO₄S : C, 68.1; H, 4.7; O, 15.8; Found: C, 68.0; H, 4.4; O, 15.5 %

HRMS (ESI MS) *m/z*: theor: 405.1035 found: 405.1036 (M⁺ detected).

Synthesis of ethyl 4-((6-bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylate (dye 6)



Chemical Formula: C₂₂H₂₂BrNO₄
Molecular Weight: 444.3250

4-((6-Bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylic acid¹ (5 g, 12.01 mmol, M = 416.27 g/mol) was suspended in ethanol and a few drops of concentrated sulfuric acid was added. The reaction was refluxed for two days. After cooling, the solvent was removed under reduced pressure. The residue was dissolved in DCM and saturated aq. Na₂CO₃ was added. The organic phase was washed several times with water, dried over magnesium sulfate and the solvent removed under reduced pressure. Addition of a

¹ M. Rahal, H. Mokbel, B. Graff, V. Pertici, D. Gimes, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, ChemPhotoChem 5 (2021) 476–490.

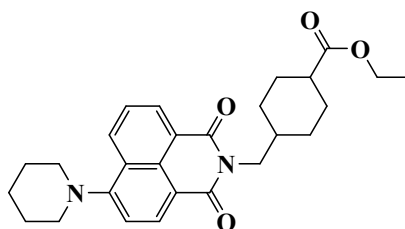
minimum of DCM followed by pentane precipitated a light-yellow solid that was filtered off, washed several times with pentane and dried under vacuum (4.48 g, 84% yield).

^1H NMR (400 MHz, DMSO- d_6) δ 8.65 (dd, $J = 7.3, 1.1$ Hz, 1H), 8.57 (dd, $J = 8.5, 1.1$ Hz, 1H), 8.41 (d, $J = 7.9$ Hz, 1H), 8.04 (d, $J = 7.9$ Hz, 1H), 7.84 (dt, $J = 11.1, 5.5$ Hz, 1H), 4.12 – 4.04 (m, 4H), 2.24 (tt, $J = 12.2, 3.6$ Hz, 1H), 2.03 – 1.77 (m, 5H), 1.44 – 1.32 (m, 2H), 1.27 – 1.11 (m, 5H)

^{13}C NMR (101 MHz, DMSO- d_6) δ 175.87, 163.94, 163.91, 133.28, 132.16, 131.35, 131.12, 130.66, 130.27, 129.07, 128.09, 123.05, 122.18, 60.11, 45.89, 43.25, 36.12, 29.98, 28.45, 14.20

HRMS (ESI MS) m/z : theor: 443.0732 found: 443.0734 (M^+ detected)

Synthesis of ethyl 4-((1,3-dioxo-6-(piperidin-1-yl)-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylate (dye 7)



Chemical Formula: $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_4$
Molecular Weight: 448.5630

4-((1,3-Dioxo-6-(piperidin-1-yl)-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylic acid² (5.05 g, 12.01 mmol, $M = 420.51$ g/mol) was suspended in ethanol and a few drops of concentrated sulfuric acid was added. The reaction was refluxed for two days. After cooling, the solvent was removed under reduced pressure. The residue was dissolved in DCM and saturated aq. Na_2CO_3 was added. The organic phase was washed several times with water, dried over magnesium sulfate and the solvent removed under reduced pressure. Addition of a minimum of DCM followed by pentane precipitated a light-yellow solid that was filtered off, washed several times with pentane and dried under vacuum (4.90 g, 91% yield).

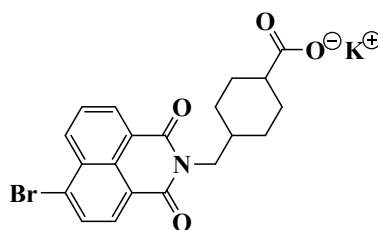
² M. Rahal, H. Mokbel, B. Graff, V. Pertici, D. Gimes, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, ChemPhotoChem 5 (2021) 476–490.

^1H NMR (400 MHz, CDCl_3) δ 8.59 (t, $J = 7.6$ Hz, 2H), 8.46 (d, $J = 7.9$ Hz, 1H), 7.74 (dd, $J = 8.3, 7.4$ Hz, 1H), 7.54 (d, $J = 7.9$ Hz, 1H), 4.06 (d, $J = 7.0$ Hz, 2H), 3.14 (t, $J = 7.2$ Hz, 2H), 2.36 – 2.21 (m, 1H), 2.02 (d, $J = 11.3$ Hz, 4H), 1.95 – 1.74 (m, 6H), 1.39 (dd, $J = 25.5, 10.8$ Hz, 4H), 1.28 – 1.06 (m, 8H)

Anal. Calc. for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_4$: C, 72.3; H, 7.2; O, 14.3; Found: C, 72.1; H, 7.4; O, 14.5 %

HRMS (ESI MS) m/z : theor: 448.2362 found: 448.2358 (M^+ detected)

Synthesis of potassium 4-((6-bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylate (dye 8)



Chemical Formula: $\text{C}_{20}\text{H}_{17}\text{BrKNO}_4$
Molecular Weight: 454.3613

4-((6-Bromo-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylic acid³ (2 g, 4.80 mmol, $M = 416.27$ g/mol) was dissolved in a mixture THF:water 1:1 and a diluted solution of aq. KOH was added. The reaction was stirred at room temperature for one hour. THF was removed under reduced pressure. Upon concentration of the aqueous phase, a precipitate formed. It was filtered off, washed several times with THF and dried under vacuum (1.70 g, 78% yield).

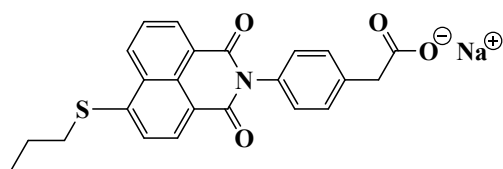
^1H NMR (400 MHz, D_2O) δ 7.88 – 7.81 (m, 1H), 7.76-7.71 (m, 1H), 7.65-5.59 (m, 1H), 7.53 (d, $J = 7.0$, 1H), 7.43 (d, $J = 7.9$ Hz, 1H), 3.17 (d, $J = 6.4$ Hz, 1H), 2.86 – 2.80 (m, 1H), 2.10-2.02 (m, 2H), 1.90 – 1.73 (m, 2H), 1.68-1.57 (m, 2H), 1.36 – 1.19 (m, 2H), 1.07 – 0.93 (m, 2H).

Anal. Calc. for $\text{C}_{20}\text{H}_{17}\text{BrKNO}_4$: C, 52.9; H, 3.8; O, 14.1; Found: C, 53.1; H, 3.4; O, 14.5 %

³ M. Rahal, H. Mokbel, B. Graff, V. Pertici, D. Gimes, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, ChemPhotoChem 5 (2021) 476-490.

HRMS (ESI MS) m/z: theor: 454.3618 found: 454.3612 (M⁻ detected)

Synthesis of sodium 2-(4-(1,3-dioxo-6-(propylthio)-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)phenyl)acetate (dye 9)



Chemical Formula: C₂₃H₁₈NNaO₄S
Molecular Weight: 427.4498

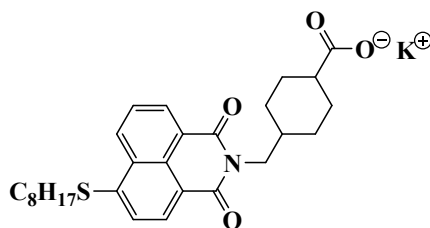
4-((1,3-Dioxo-6-(propylthio)-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylic acid (1.5 g, 3.64 mmol, M = 411.52 g/mol) were dissolved in THF (40 mL) and aq. KOH (40%, 2 mL) were added. The solution was stirred at room temperature for one hour. The solvent was removed under reduced pressure. Addition of THF precipitated a brown solid that was filtered off, washed several times with pentane and dried under vacuum (1.03 g, 66% yield).

¹H NMR (400 MHz, D₂O) δ 8.54 (brs, 1H), 8.28 (brs, 1H), 7.84 (brs, 1H), 7.59 (brs, 1H), 7.46 (brs, 1H), 7.12 (brs, 2H), 6.74 (brs, 2H), 3.71 (brs, 2H), 3.18 (brs, 2H), 1.87-1.84 (m, 2H), 0.93 (brs, 3H)

Anal. Calc. for C₂₃H₁₈NNaO₄S : C, 64.6; H, 4.2; O, 15.0; Found: C, 64.6; H, 4.4; O, 15.5 %

HRMS (ESI MS) m/z: theor: 427.4503 found: 427.4501 (M⁻ detected)

Synthesis of potassium 4-((6-(octylthio)-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylate (dye 10)



Chemical Formula: C₂₈H₃₄KNO₄S
Molecular Weight: 519.7413

4-((6-(octylthio)-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylic acid (2 g, 4.15 mmol, M = 481.65 g/mol) was dissolved in a mixture THF:water 1:1 and a diluted solution of aq. KOH was added. The reaction was stirred at room temperature for one hour. THF was removed under reduced pressure. Upon concentration of the aqueous phase, a precipitate formed. It was filtered off, washed several times with THF and dried under vacuum (1.75 g, 81% yield). Analyses were consistent with those previously reported in the literature for sodium 4-((6-(octylthio)-1,3-dioxo-1*H*-benzo[*de*]isoquinolin-2(3*H*)-yl)methyl)cyclohexane-1-carboxylate [M. Rahal, H. Mokbel, B. Graff, V. Pertici, D. Gimes, J. Toufaily, T. Hamieh, F. Dumur, J. Lalevée, ChemPhotoChem 5 (2021) 476-490].

¹H NMR (400 MHz, D₂O) δ : 7.95-7.89 (brs, 1H), 7.70-7.62 (brs, 1H), 7.58-7.50 (brs, 1H), 7.23-7.15 (brs, 1H), 6.85-6.77 (brs, 1H), 3.65-3.50 (brs, 2H), 2.85-2.65 (brs, 2H), 2.15-2.03 (brs, 1H), 1.95-1.80 (m, 2H), 1.75-1.50 (m, 4H), 1.48-1.11 (m, 15H), 0.92 (t, 8.6 Hz, 3H)

Anal. Calc. for C₂₈H₃₄KNO₄S : C, 64.7; H, 6.6; O, 12.3; Found: C, 65.0; H, 6.4; O, 12.5 %

HRMS (ESI MS) m/z: theor: 480.2214 found: 480.2210 (M⁻ detected).