Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

New versatile bimolecular photoinitating systems based on amino-*m*-terphenyl derivatives for cationic, free radical and thiol-ene photopolymerization under low intensity UV-A and visible lights sources

Emilia Hola[1], Maciej Pilch[1], Mariusz Galek[2], Joanna Ortyl[1,2 *]

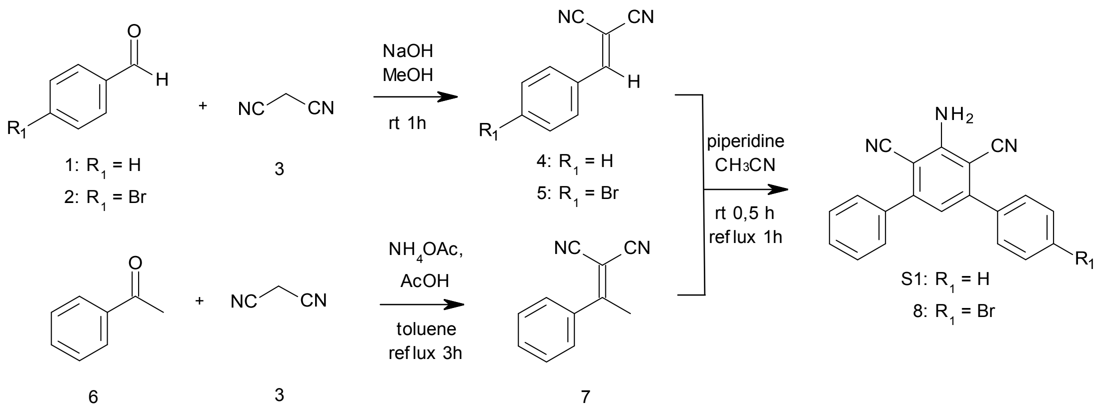
[1] Department of Biotechnology and Physical Chemistry, Faculty of Chemical Engineering and Technology, Cracow University of Technology, Warszawska 24, 31-155 Cracow, Poland

[2] Photo HiTech Ltd., Bobrzyńskiego 14, 30-348 Cracow, Poland

Corresponding author: jortyl@chemia.pk.edu.pl

Synthesis of 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives

All reagents and solvents were purchased from Aldrich, Alfa Aesar or Fluorochem and used as received without further purification. Structure and purity of obtained products were confirmed by NMR and LC-MS analysis. ^{1}H NMR spectra were recorded in DMSO-D_6 on Avance III HD 400 MHz (Bruker) spectrometer. Chemical shifts are reported in parts per million (δ) and referenced to residual protonated solvent (DMSO) peak (δ = 2.50 ppm). LC-MS analyses were obtained on Waters Acquity TQD equipped with a quadrupole detector and with ESI ionization method. Absorbance measurement during LC-MS analyses in the range of 200-700 nm. Acetonitrile was used as an eluent.



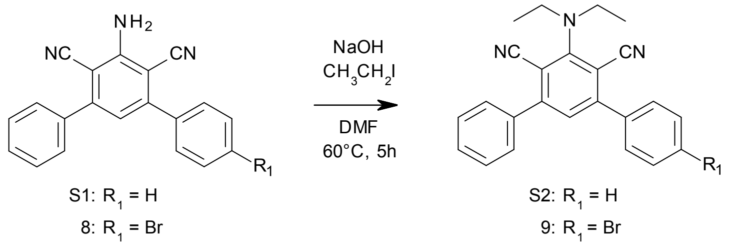
Scheme S-1. The synthetic procedure for the preparation of 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives.

Aldehyde 1 (108 mmol, 11.45 g) or 2 (54 mmol, 20.00 g) and malononitrile 3 (129.6 mmol, 8.56 g) were dissolved in methanol (35 cm^3), an aqueous solution of NaOH (0.54 mmol, 22.0 mg in 6 cm^3 of water) was added dropwise and the mixture was stirred at room temperature for one hour. To the obtained precipitate methanol (10 cm^3) was added and crystallization was carried out. The resulting precipitate was filtered under reduced pressure, washed with cold methanol and dried under vacuum (4: 14.8 g, 89%, 5: 23.7 g, 94%)

Acetophenone (83 mmol, 10.0 g) and malononitrile 3 (166.6 mmol, 10.99 g) were dissolved in toluene (200 cm^3), then ammonium acetate (17 mmol, 1.28 g) and acetic acid (20 cm^3) were added. The resulting mixture was heated under reflux under a Dean-Stark trap for 4 hours. The solvent was evaporated and water was added to the remaining oil and it was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4. After evaporation of the solvent, crystallization from methanol was carried out, the obtained precipitate was filtered under reduced pressure and dried under vacuum (7: 10.14 g, 72%)

Compounds 4 (47.8 mmol, 7.36 g) or 5 (47.8 mmol, 11.15 g) and 7 (47.8 mmol, 8.04 g) were suspended in acetonitrile (100 cm^3) and piperidine (6.95 cm^3) was added.[1 2] The mixture was stirred at room temperature for one hour, then at the reflux temperature for one hour. After cooling the reaction mixture, the obtained precipitate was filtered under reduced pressure, washed with cold acetonitrile and dried under vacuum (S1: 14.30 g, 80%, 8: 12.00 g, 67%)

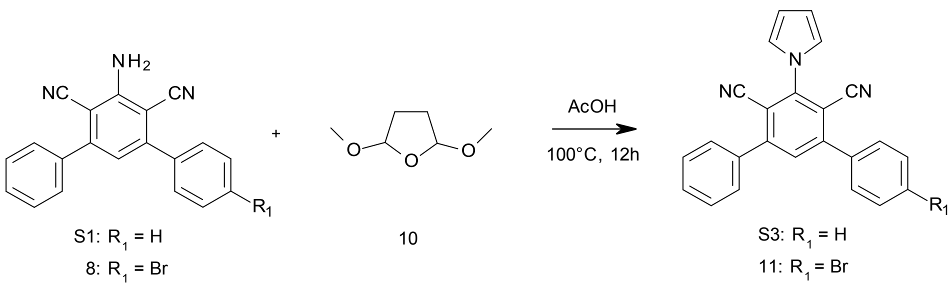
Synthesis of 2-diethylamino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives.



Scheme S-2. The synthetic procedure for the preparation of 2-diethylamino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives.

S1 (8 mmol, 2.37 g) or 8 (8mmol, 3.00 g) was dissolved in DMF (66.0 cm^3), sodium hydroxide (26,45 mmol, 1.06 g) was added, followed by iodoethane (34 mmol, 3.18 cm^3), the mixture was heated for 5 hours at 60°C. Then water was added and mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The product was purified by column chromatography (SiO_2, hexane / ethyl acetate), S2: 2,37 g, 84 %, 9: 2.56 g, 75%)

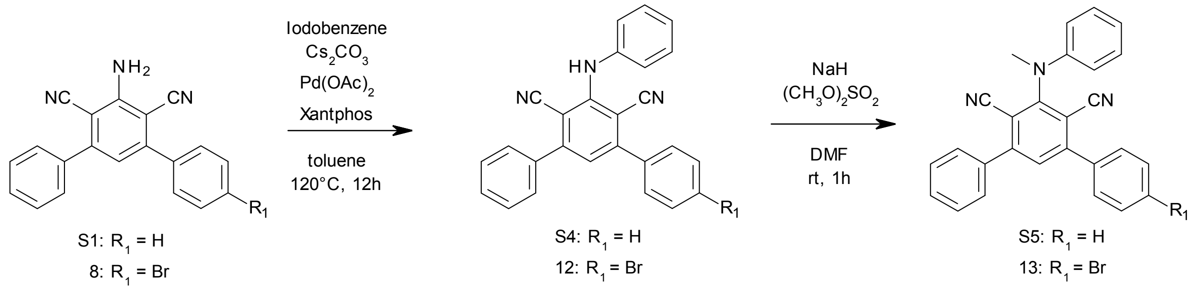
Synthesis of 4,6-diphenyl-2-pyrrol-1-yl-benzene-1,3-dicarbonitrile derivatives.



Scheme S-3. The synthetic procedure for the preparation of 4,6-diphenyl-2-pyrrol-1-yl-benzene-1,3-dicarbonitrile derivatives.

S1 (8 mmol, 2.36 g) or 8 (8 mmol, 3.00 g) was mixed with acetic acid (15.0 cm^3), then 2,5-dimethoxytetrahydrofuran (16 mmol, 2.08 cm^3) was added and stirred at 100°C for 12 hours. Then water was added and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, the solvent was evaporated under vacuum, the resulting product was crystallized from ethyl acetate/hexane (S3: 2.43 g, 88%, 11: 2.96 g, 87%).

Synthesis of 2-(N-methylanilino)-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives

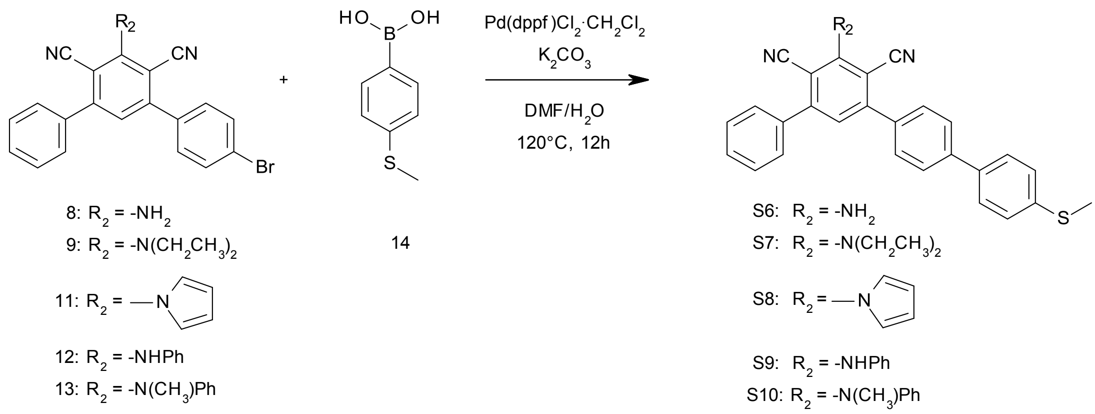


Scheme S-4. The synthetic procedure for the preparation of 2-(N-methylanilino)-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives.

S1 (1.34 mmol, 395.0 mg) or 8 (1.34 mmol, 500.0 mg), iodobenzene (2.14 mmol, 0.240 cm^3), Cs_2CO_3 (1.88 mmol, 611 mg), a palladium catalyst consisting of with $Pd(OAc)_2$ (0.07 mmol, 15.0 mg) and (Xantphos) (0.07 mmol, 39.0 mg), anhydrous toluene (10 cm^3) were placed in oven-dried seal tube under argon and stirred 12h at 120°C. Then water was added and mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated and purified by column chromatography (SiO2, hexane / ethyl acetate), (S4: 457.0 mg, 92%, 112: 298 mg, 60%).

S4 (0.49 mmol, 182.0 mg) or 12 (0.49 mmol, 220.0 mg) was dissolved in DMF (5.3 cm^3) at 0°C, NaH (0.98 mmol, 24.0 mg) was added and stirred for 30 min. Dimethyl sulphate (1.46 mmol, 0.139 cm^3) was added and stirred for 1 h at room temperature. Then water was added and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, concentrated and purified by column chromatography (SiO_2, hexane/ethyl acetate), (S5: 164.0 mg, 87%, 13: 155.0 mg, 70%).

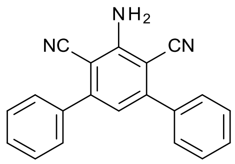
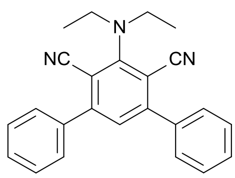
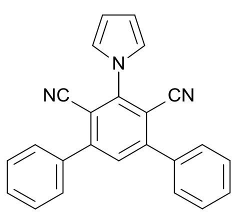
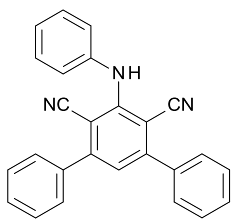
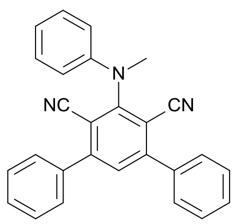
Synthesis of 2-amino-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile derivatives.

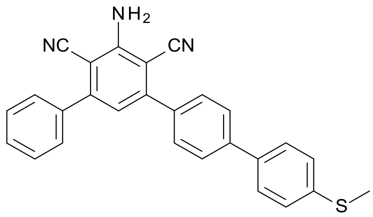
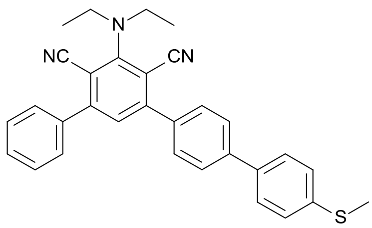
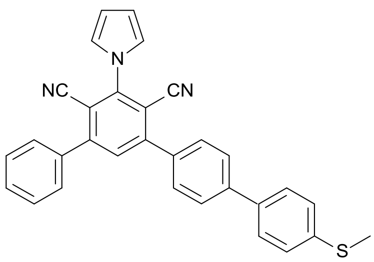
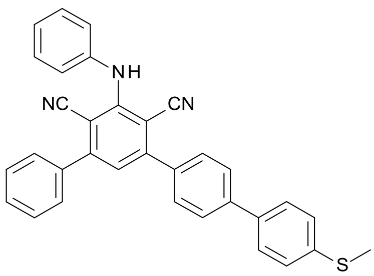
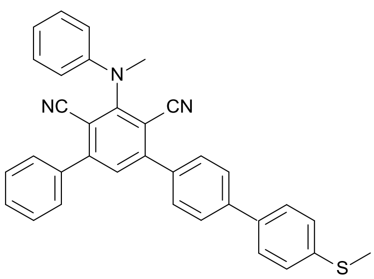


Scheme S-5. The synthetic procedure for the preparation of 2-amino-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile derivatives.

Appropriate compound 8 (0.22 mmol, 82.00 mg), 9 (0.22 mmol, 100.00 mg), 11 (0.22 mmol, 95.00 mg), 12 (0.22mmol, 100.00 mg) or 13 (0.22 mmol, 100.0 mg), 4-(methylthio)phenylboronic acid (0.26 mmol, 39.00 mg), potassium carbonate (0.32 mmol, 45.00 mg) and palladium catalyst $Pd(dppf)Cl_2 \cdot CH_2Cl_2$ (0.01m mol, 9.00 mg) were suspended in DMF (1.5 cm^3) and water (0.3 cm^3). Mixture was purged with argon and heated 12h at 120°C. Then water was added and mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The purification was performed via column chromatography (SiO_2, hexane / ethyl acetate) (S6: 50.00 mg, 55% S7: 83.0 mg, 75%, S8: 90.00 mg, 86%, S9: 72 .00mg, 65% S10: 96.00 mg, 87%)

Structure and purity of obtained products confirmed by NMR and LC-MS analysis.

 **S1**	**2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile** Yield: 80% ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78-7.73 (m, 2H), 7.70-7.64 (m, 4H), 7.58-7.52 (m, 4H), 7.40(s, 1H), 6.90-6.83 (s, 2H) MS (ESI) m/z(%): 294 ($[M-H]^-$, 100%
 **S2**	**2-(diethylamino)-4,6-diphenyl-benzene-1,3-dicarbonitrile** Yield: 84% ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78-7.74 (m, 2H), 7.72-7.65 (m, 4H), 7.58-7.53 (m, 4H), 7.40 (s, 1H), 7.58 (q, 4H), 1.16 (t, 6H) MS (ESI) m/z(%): 352 ($[M+H]^+$, 100%
 **S3**	**4,6-diphenyl-2-pyrrol-1-yl-benzene-1,3-dicarbonitrile** Yield: 88% ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86-7.79 (m,3H), 7.77-7.71 (d.2H), 7.64-7.56 (m,4H), 7.44-7.32 (m,4H), 6.44-6.38 (t, 2H), MS (ESI) m/z(%): 344 ($[M+H]^+$, 100%
 **S4**	**2-anilino-4,6-diphenyl-benzene-1,3-dicarbonitrile** Yield: 92% ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.13 (s, 1H), 7.72-7.68 (m, 4H), 7.60-7.49 (m, 6H), 7.40 (s,1H), 7.30 (t,2H), 7.10 (d, 2H), 6.99 (t, 1H) MS (ESI) m/z(%): 412 ($[M+CH_3CN]^+$, 100%
 **S5**	**2-(N-methylanilino)-4,6-diphenyl-benzene-1,3-dicarbonitrile** Yield: 87% ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.79-7.72(m, 5H), 7.61-7.54 (m, 6H), 7.26 (t, 2H), 6.87 (t,1H), 6.80 (d, 2H), 3.5 (s, 3H) MS (ESI) m/z(%): 386 ($[M+H]^+$, 94%

 **S6**	**2-amino-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile** Yield: 55% ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.83 (d, 2H), 7.76-7.71 (m, 4H), 7.68-7.64 (m, 2H), 7.56-7.52 (m, 3H), 7.38 (d, 2H), 6.85 (m, 3H), 2.54 (s, 3H) MS (ESI) m/z(%): 416 ($[M-H]^-$, 96%
 **S7**	**2-(diethylamino)-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile** Yield: 75% ^{1}H NMR (400 MHz, DMSO-d_6) δ 7,88-7,77 (dd,4H), 7.77-7.69 (m, 4H), 7.60-7.51 (m, 3H), 7.46-7.41 (s, 1H), 7.41-7.34 (d, 2H), 3.66-3.54 (q, 4H), 2.55 (s,3H), 1.21-1.11 (t, 6H) MS (ESI) m/z(%): 474 ($[M+H]^+$, 100%
 **S8**	**4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-2-pyrrol-1-yl-benzene-1,3-dicarbonitrile** Yield: 86% ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96-7.86 (m, 5H), 7.86-7.79 (m,2H), 7.77-7.71 (d,2H), 7.64-7.56 (m,3H), 7.44-7.32 (m,4H), 6.44-6.38 (t, 2H), 2.53 (s, 3H) MS (ESI) m/z(%): 468 ($[M+H]^+$, 100%
 **S9**	**2-anilino-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile** Yield: 65% ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 7.92-7.75 (m, 4H), 7.70-7.63 (m, 5H), 7.60-7.51 (m, 4H), 7.47-7.35 (m, 3H) 7.34-7.24 (t, 1H), 7.10 (d, 2H), 2.54 (s, 3H) MS (ESI) m/z(%): 535 ($[M+CH_3CN]^+$, 100%
 **S10**	**2-(N-methylanilino)-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile** Yield: 87% ^{1}H NMR (400 MHz, DMSO) δ 7.91 – 7.81 (m, 5H), 7.81 – 7.70 (m, 4H), 7.64 – 7.54 (m, 3H), 7.39 (d, 2H), 7.33 – 7.23 (m, 2H), 6.88 (t,1H), 6.81 (d, 2H), 3.51 (s, 3H), 2.53 (s, 3H) MS (ESI) m/z(%): 508 ($[M+H]^+$, 94%

Steady state photolysis for the 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives in acetonitrile.

WITHOUT IODONIUM SALT during 30 minutes

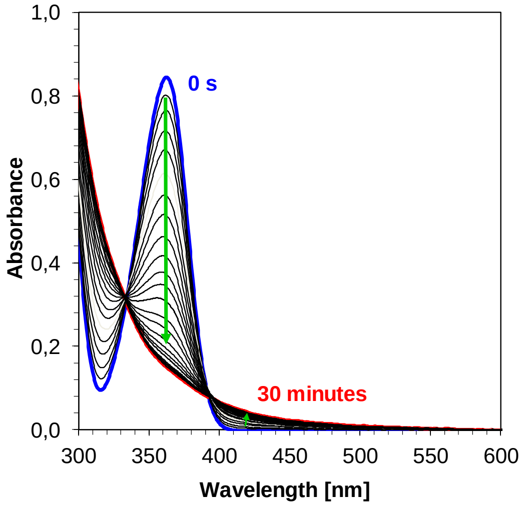


Fig. S1 Photolysis of S1 in acetonitrile under 365nm (190mW/cm^2); concentration [S1] = 6,78·10^{-5} [mol/dm^3].

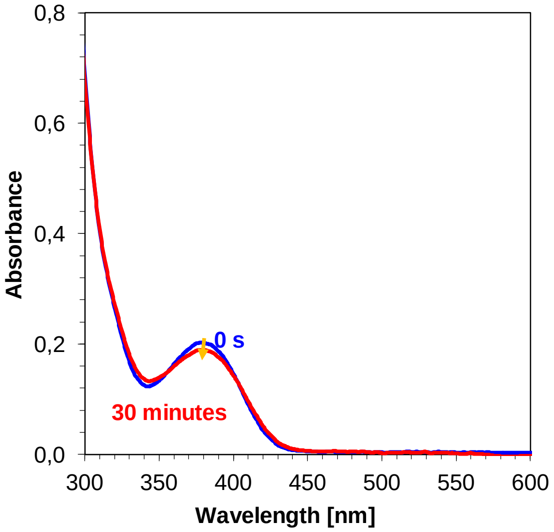


Fig. S3 Photolysis of S2 in acetonitrile under 365nm (190mW/cm^2); concentration [S2] = 4,04·10^{-5} [mol/dm^3].

WITH IODONIUM SALT – SPEEDCURE 938 during 10 minutes

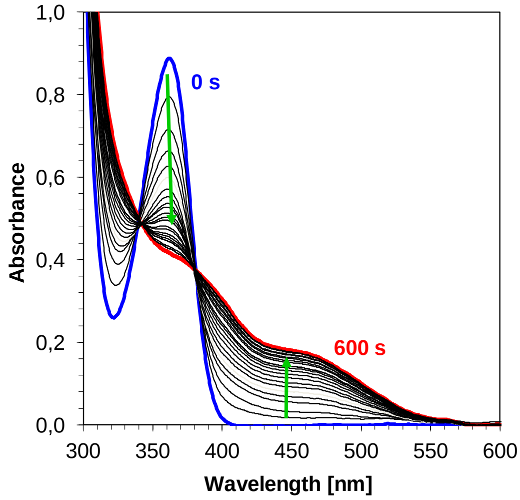


Fig. S2 Photolysis of S1 with Speedcure 938 iodonium salt in acetonitrile under 365nm (190mW/cm^2); concentration [S1] = 6,78·10^{-5} [mol/dm^3] and concentration Speedcure 938 [IOD] = 1,59·10^{-3} [mol/dm^3].

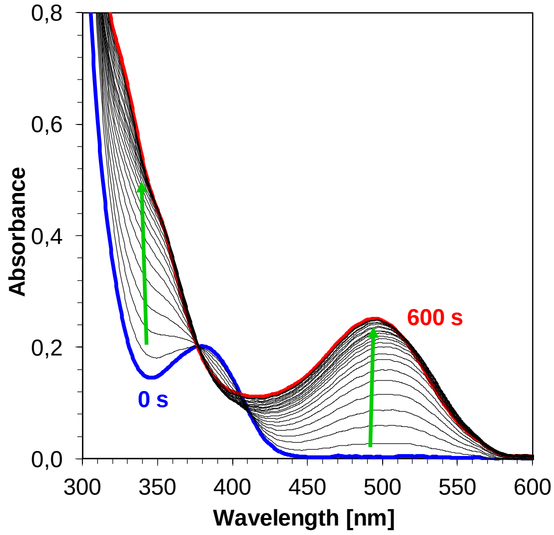


Fig. S4 Photolysis of S2 with Speedcure 938 iodonium salt in acetonitrile under 365nm (190mW/cm^2); concentration [S2] = 4,04·10^{-5} [mol/dm^3] and concentration Speedcure 938 [IOD] = 1,59·10^{-3} [mol/dm^3].

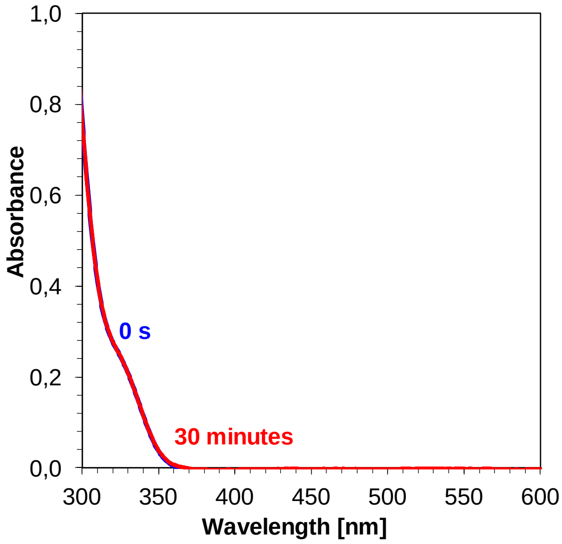


Fig. S5 Photolysis of S3 in acetonitrile under 365nm (190mW/cm^2); concentration [S3] = 3,42·10^{-5} [mol/dm^3].

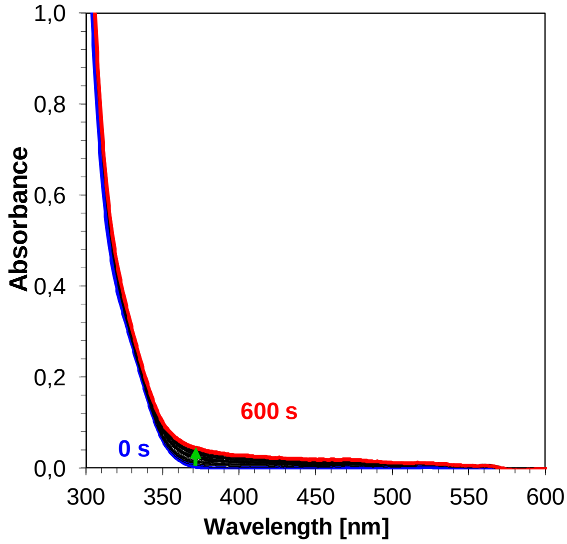


Fig. S6 Photolysis S3 with Speedcure 938 iodonium salt in acetonitrile under 365nm (190mW/cm^2); concentration [S3] = 3,42·10^{-5} [mol/dm^3] and concentration Speedcure 938 [IOD] = 1,59·10^{-3} [mol/dm^3].

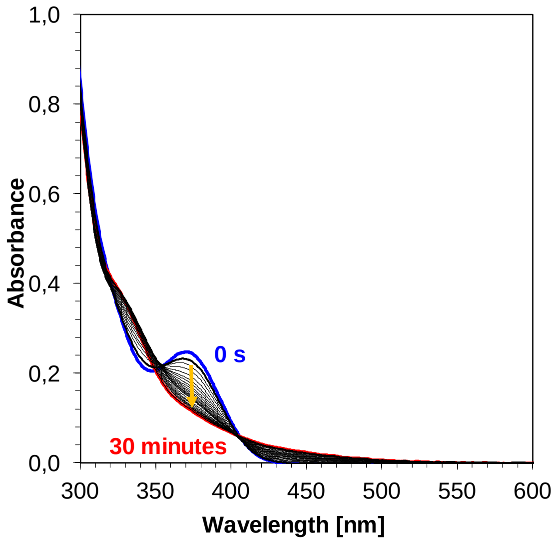


Fig. S7 Photolysis of S4 in acetonitrile under 365nm (190mW/cm^2); concentration [S4] = 3,26·10^{-5} [mol/dm^3].

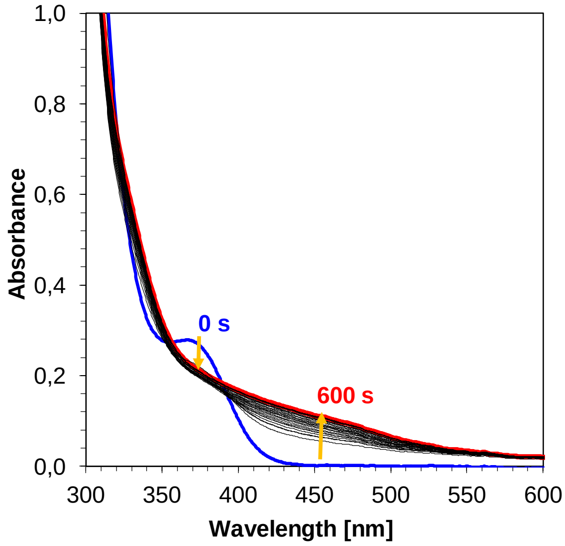


Fig. S8 Photolysis of S4 with Speedcure 938 iodonium salt in acetonitrile under 365nm (190mW/cm^2); concentration [S4] = 3,26·10^{-5} [mol/dm^3] and concentration Speedcure 938 [IOD] = 1,59·10^{-3} [mol/dm^3].

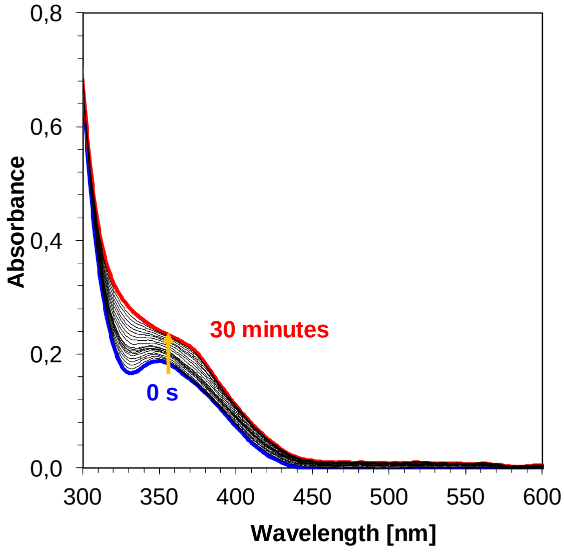


Fig. S9 Photolysis of S5 in acetonitrile under 365nm (190mW/cm^2); concentration [S5] = 5,71·10^{-5} [mol/dm^3].

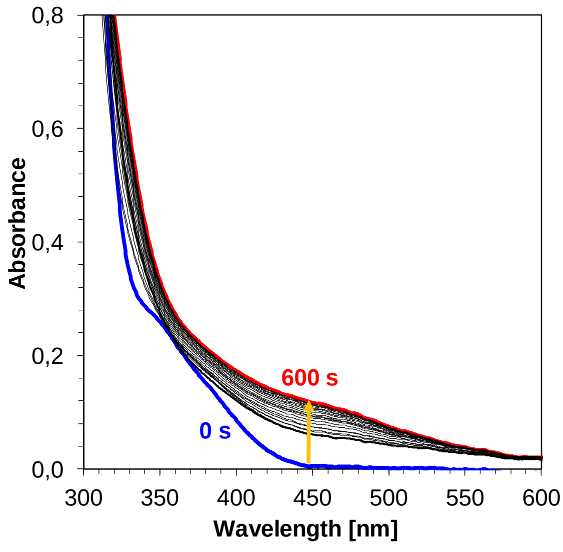


Fig. S10 Photolysis of S5 with Speedcure 938 iodonium salt in acetonitrile under 365nm (190mW/cm^2); concentration [S5] = 5,71·10^{-5} [mol/dm^3] and concentration Speedcure 938 [IOD] = 1,59·10^{-3} [mol/dm^3].

Steady state photolysis for the 2-amino-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile derivatives in acetonitrile.

WITHOUT IODONIUM SALT during 30 minutes

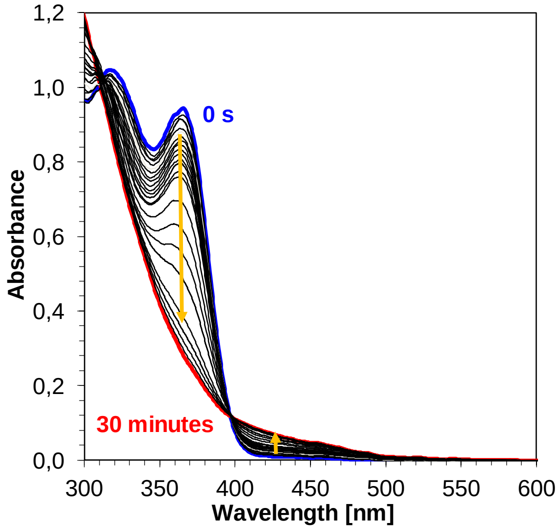


Fig. S11 Photolysis of S6 in acetonitrile under 365nm (190mW/cm^2); concentration [S6] = 5,08·10^{-5} [mol/dm^3].

WITH IODONIUM SALT – SPEEDCURE 938 during 10 minutes

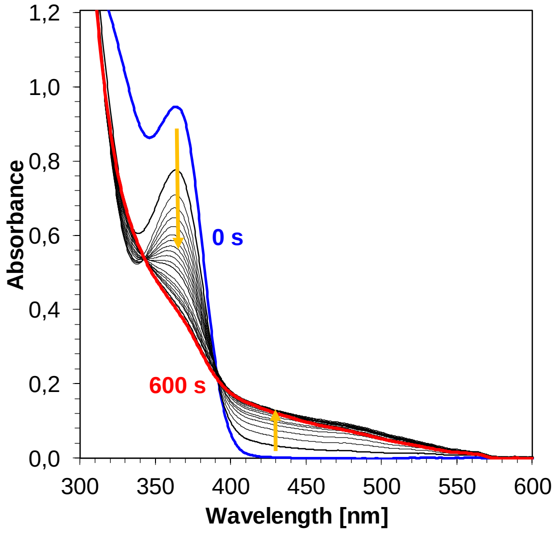


Fig. S12 Photolysis of S6 with Speedcure 938 iodonium salt in acetonitrile under 365nm (190mW/cm^2); concentration [S6] = 5,08·10^{-5} [mol/dm^3] and concentration Speedcure 938 [IOD] = 1,59·10^{-3} [mol/dm^3].

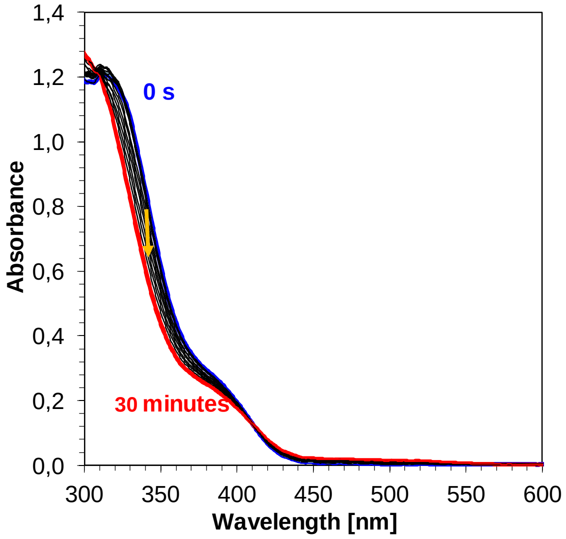


Fig. S13 Photolysis of S7 in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S7] = $4,61\cdot10^{-5}$ [mol/dm^3].

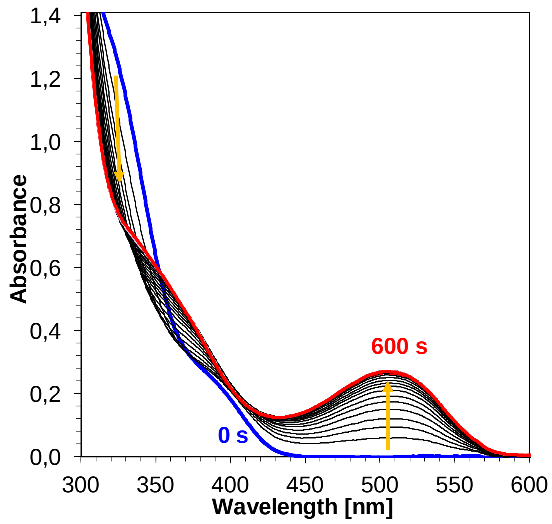


Fig. S14 Photolysis of S7 with Speedcure 938 iodonium salt in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S7] = $4,61\cdot10^{-5}$ [mol/dm^3] and concentration Speedcure 938 [IOD] =$1,59\cdot10^{-3}$ [mol/dm^3].

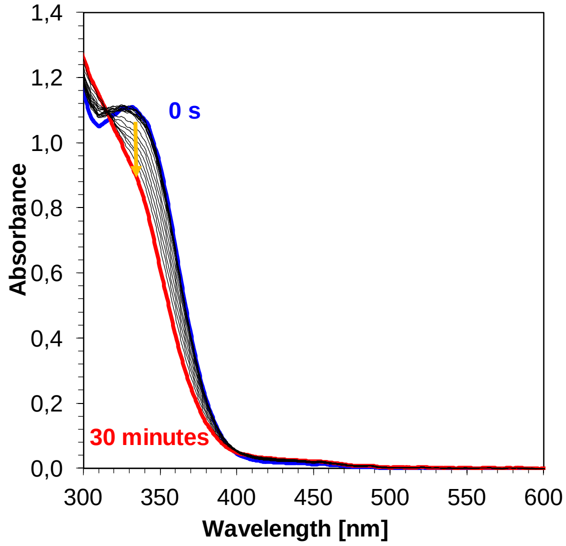


Fig. S15 Photolysis of S8 in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S8] = $4,84\cdot10^{-5}$ [mol/dm^3].

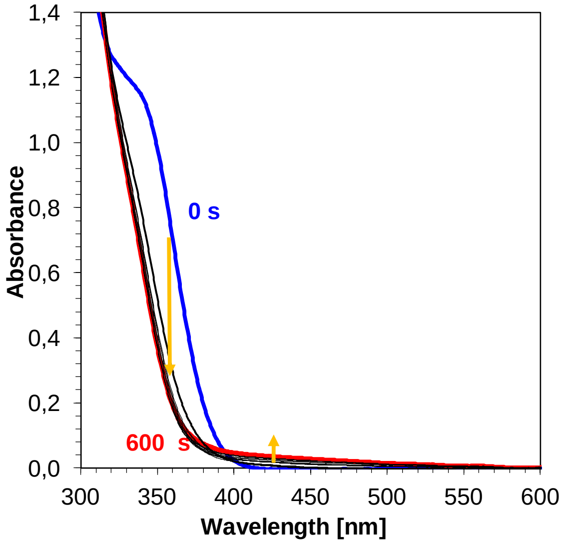


Fig. S16 Photolysis of S8 with Speedcure 938 iodonium salt in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S8] = $4,84\cdot10^{-5}$ [mol/dm^3] and concentration Speedcure 938 [IOD] = $1,59\cdot10^{-3}$ [mol/dm^3].

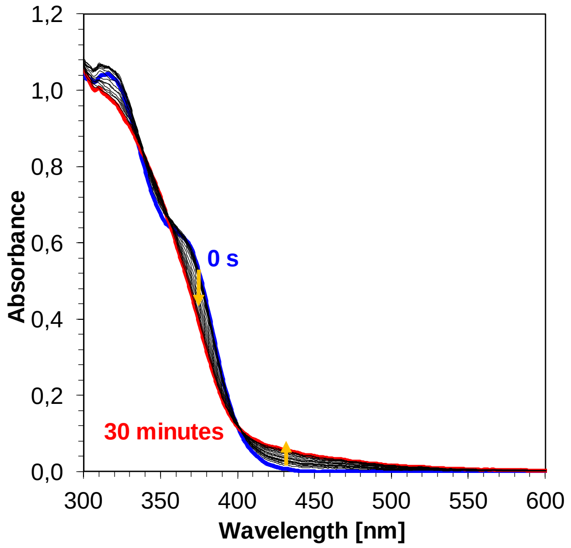


Fig. S17 Photolysis of S9 in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S9] = $4,58\cdot10^{-5}$ [mol/dm^3].

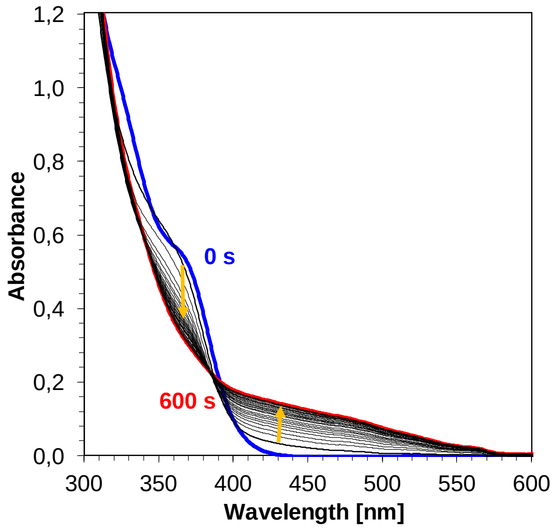


Fig. S18 Photolysis of S9 with Speedcure 938 iodonium salt in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S9] = $4,58\cdot10^{-5}$ [mol/dm^3] and concentration Speedcure 938 [IOD] = $1,59\cdot10^{-3}$ [mol/dm^3].

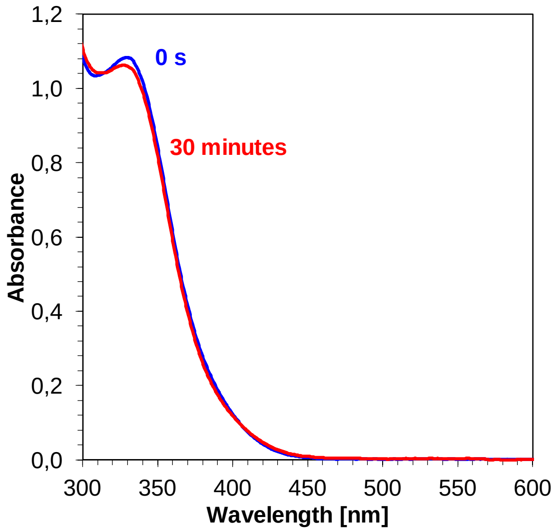


Fig. S19 Photolysis of S10 in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S10] = $4,53\cdot10^{-5}$ [mol/dm^3].

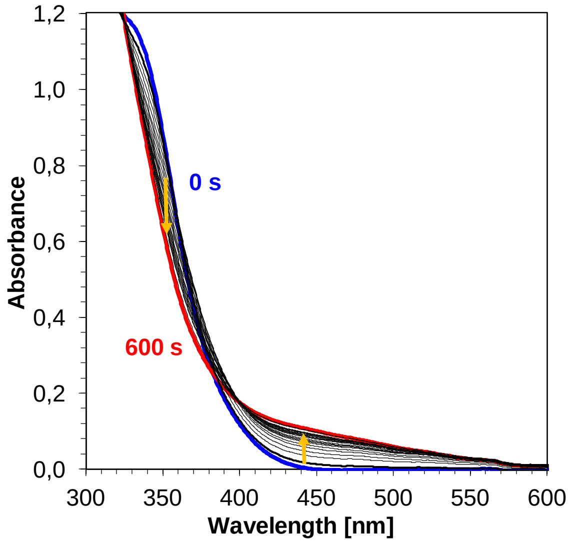


Fig. S20 Photolysis of S10 with Speedcure 938 iodonium salt in acetonitrile under 365nm ($190 mW/cm^2$); concentration [S10] = $4,53\cdot10^{-5}$ [mol/dm^3] and concentration Speedcure 938 [IOD] = $1,59\cdot10^{-3}$ [mol/dm^3].

The example of fluorescence emission quenching of the 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives by different concentrations of iodonium salt (Speedcure 938) in acetonitrile.

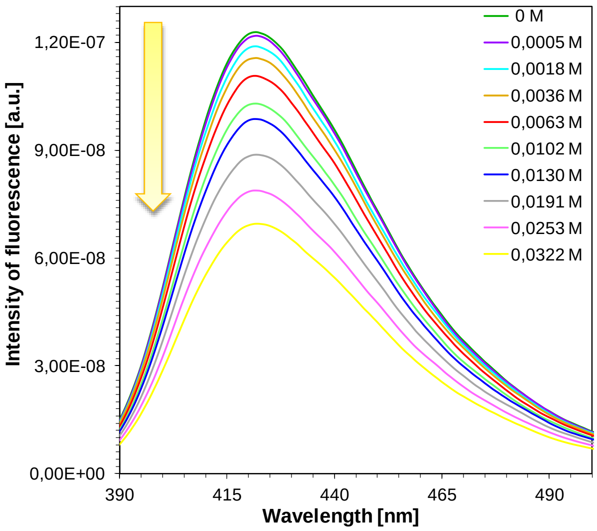


Fig. S21 Fluorescence emission quenching of S1 by different concentration of Speedcure 938 in acetonitrile; concentration [S1] = $1{,}69\cdot10^{-5}$ [mol/dm^3].

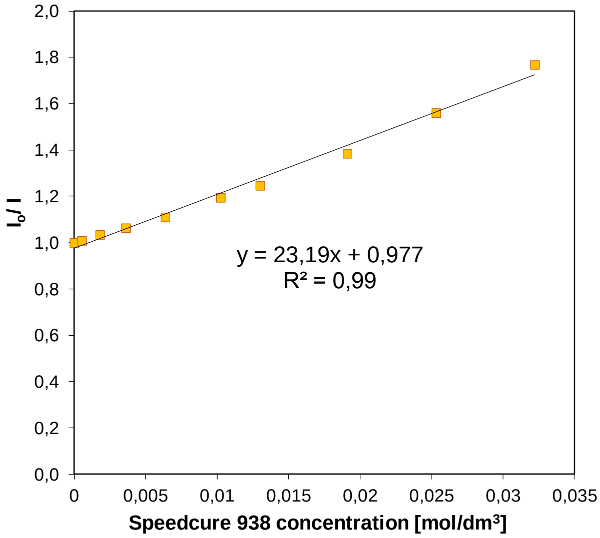


Fig. S22 Stern –Volmer plot for S1.

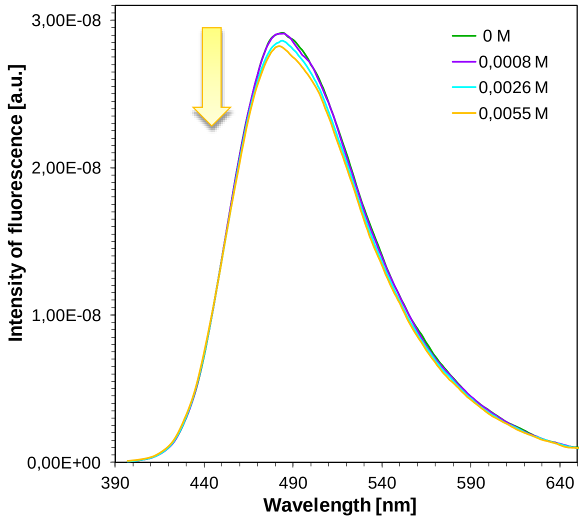


Fig. S23 Fluorescence emission quenching of S2 by different concentration of Speedcure 938 in acetonitrile; concentration [S2] = $4{,}04\cdot10^{-5}$ [mol/dm^3].

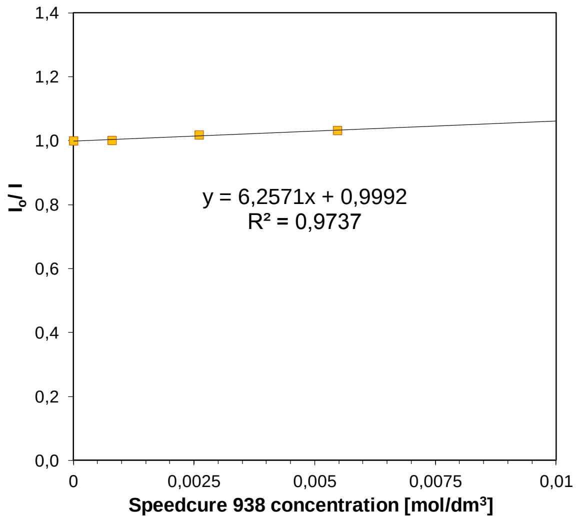


Fig. S24 Stern –Volmer plot for S2.

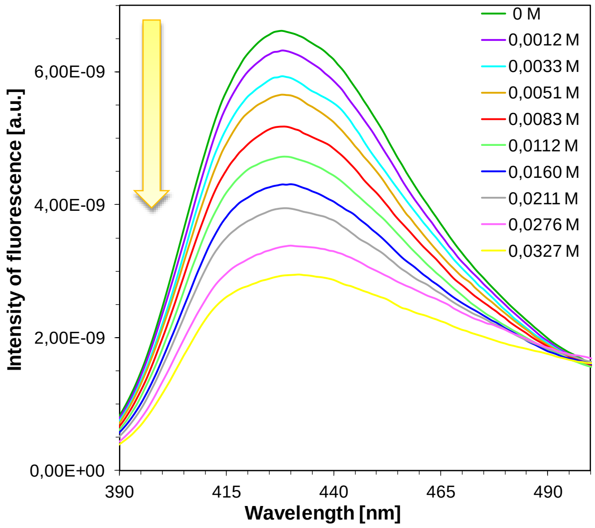


Fig. S25 Fluorescence emission quenching of S3 by different concentration of Speedcure 938 in acetonitrile; concentration [S3] = $3{,}41\cdot10^{-5}$ [mol/dm^3].

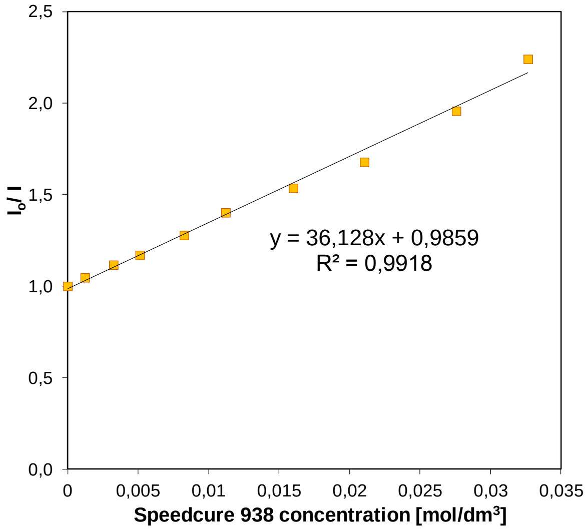


Fig. S26 Stern –Volmer plot for S3.

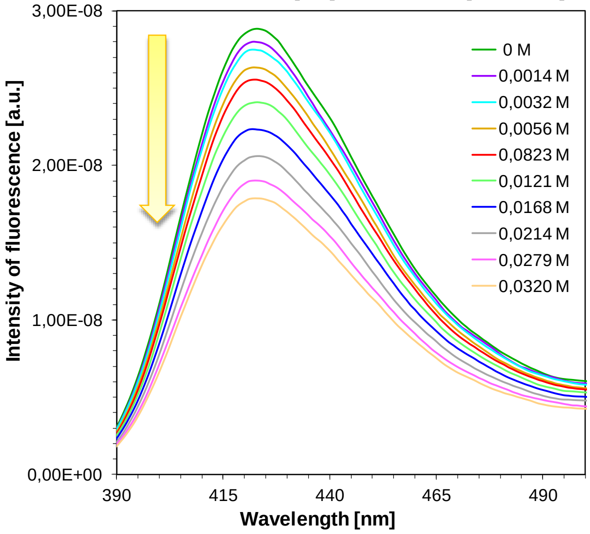


Fig. S27 Fluorescence emission quenching of S4 by different concentration of Speedcure 938 in acetonitrile; concentration [S4] = $1{,}63\cdot10^{-5}$ [mol/dm^3].

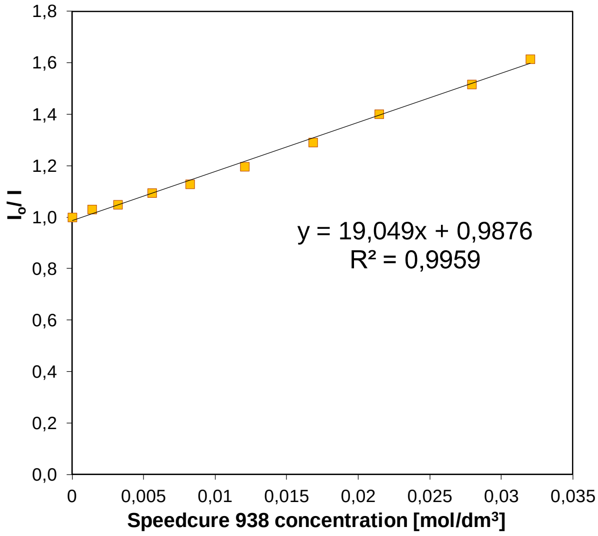


Fig. S28 Stern –Volmer plot for S4.

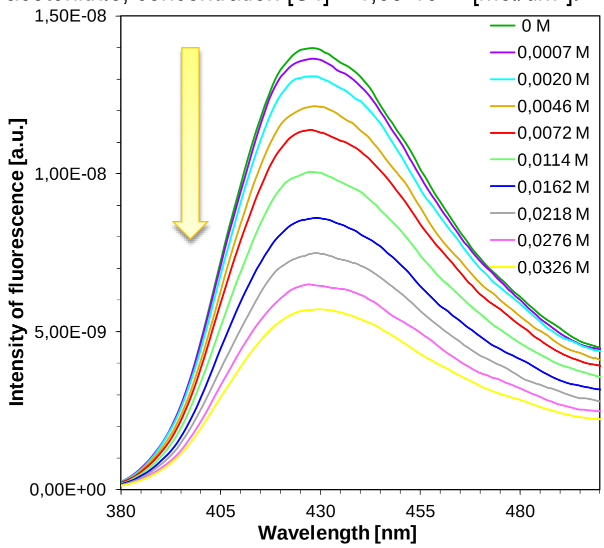


Fig. S29 Fluorescence emission quenching of S5 by

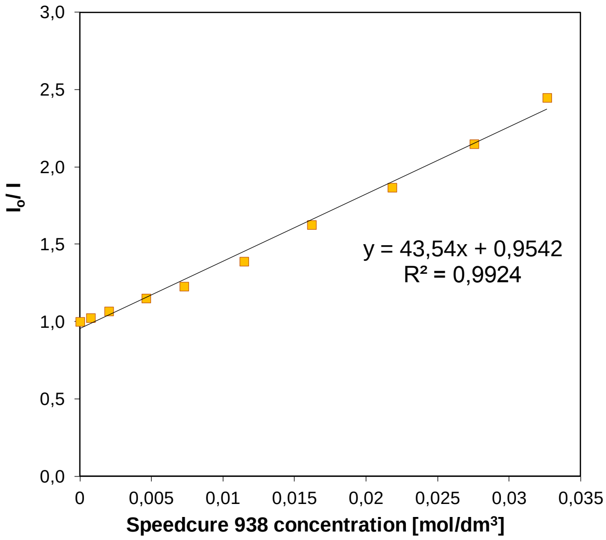


Fig. S30 Stern –Volmer plot for S5.

different concentration of Speedcure 938 in acetonitrile; concentration [S5] = 5,71·10^{-5} [mol/dm^3].

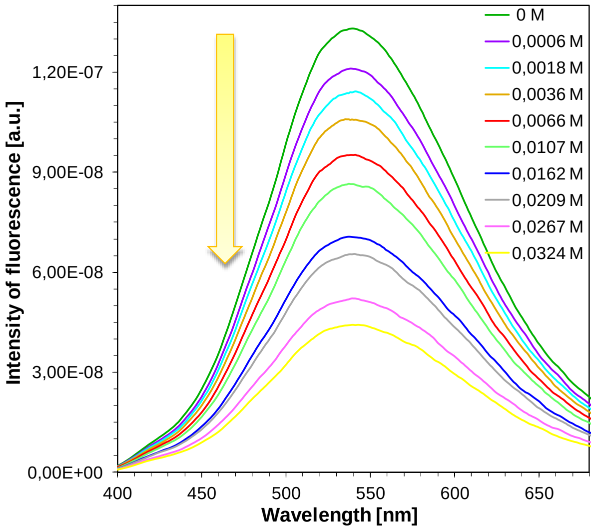


Fig. S31 Fluorescence emission quenching of S6 by different concentration of Speedcure 938 in acetonitrile; concentration [S6] = 1,02·10^{-5} [mol/dm^3].

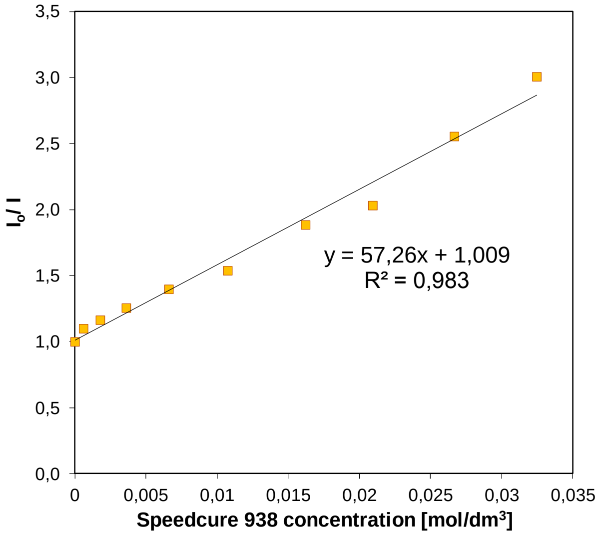


Fig. S32 Stern –Volmer plot for S6.

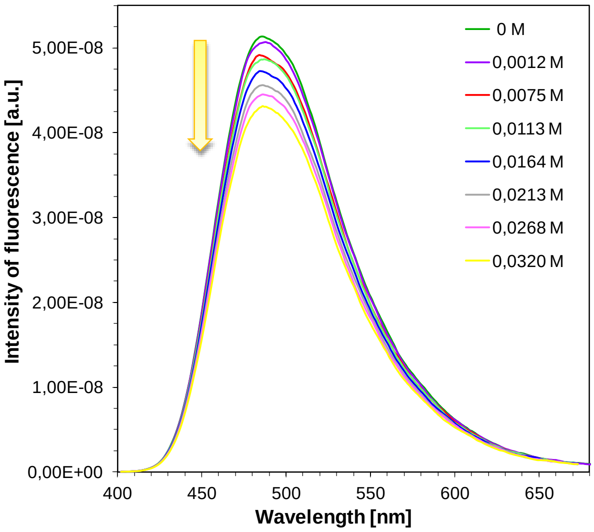


Fig. S33 Fluorescence emission quenching of S7 by different concentration of Speedcure 938 in acetonitrile; concentration [S7] = 2,30·10^{-5} [mol/dm^3].

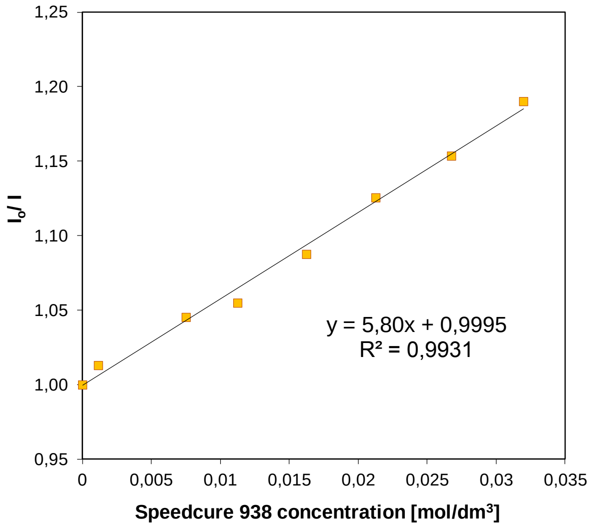


Fig. S34 Stern –Volmer plot for S7.

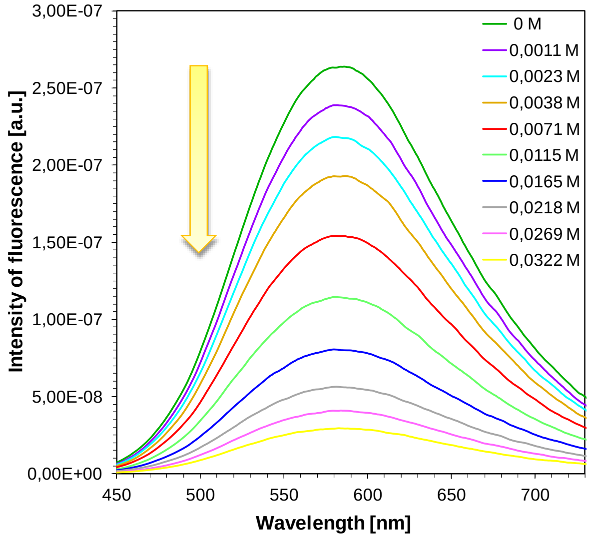


Fig. S35 Fluorescence emission quenching of S8 by different concentration of Speedcure 938 in acetonitrile; concentration [S8] = 9,68·10^{-6} [mol/dm^3].

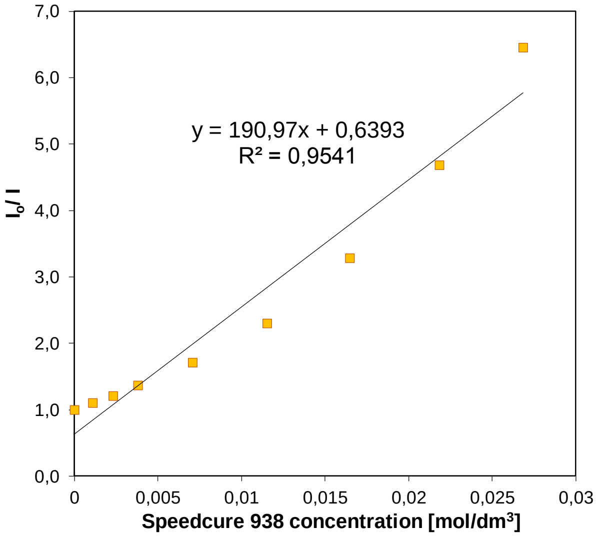


Fig. S36 Stern –Volmer plot for S8.

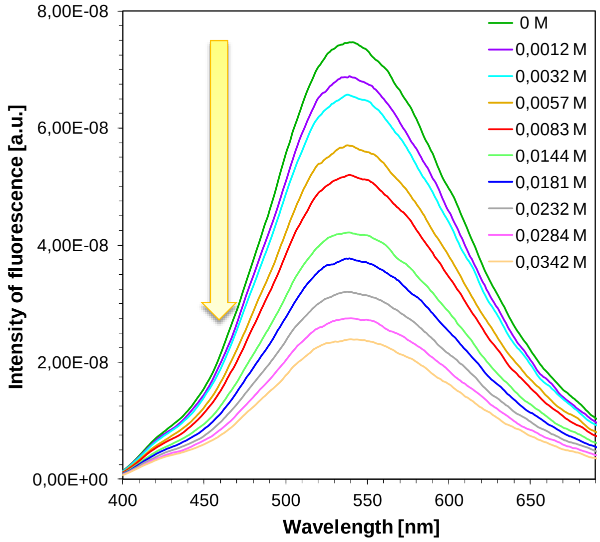


Fig. S37 Fluorescence emission quenching of S9 by different concentration of Speedcure 938 in acetonitrile; concentration [S9] = 1,53·10^{-5} [mol/dm^3].

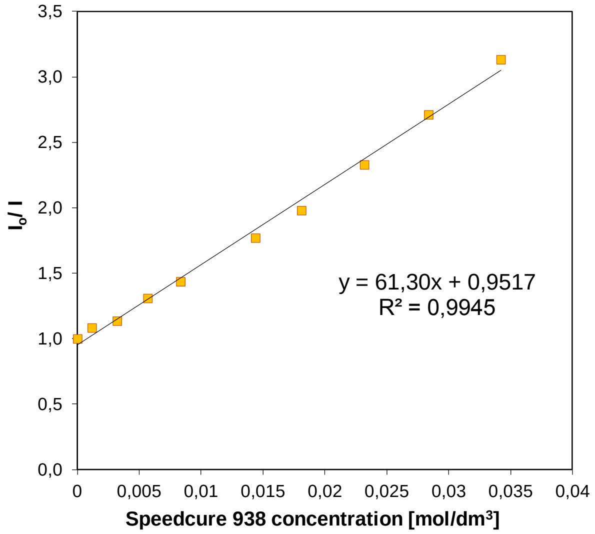


Fig. S38 Stern –Volmer plot for S9.

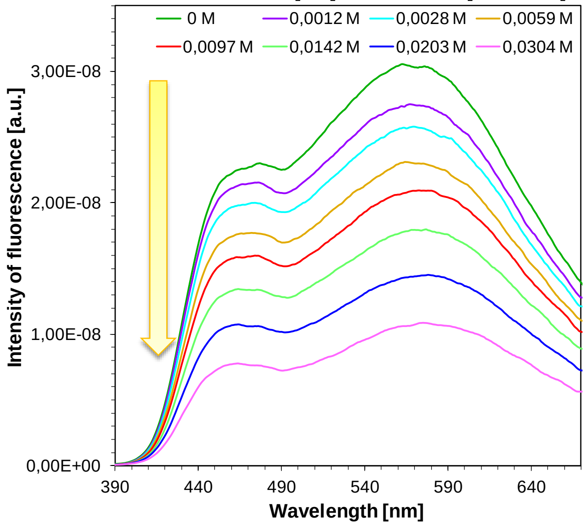


Fig. S39 Fluorescence emission quenching of S10 by

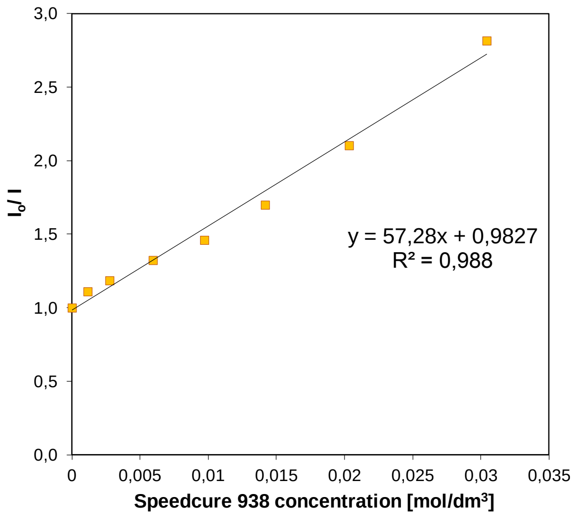


Fig. S40 Stern –Volmer plot for S10.

different concentration of Speedcure 938 in acetonitrile; concentration [S10] = $9{,}07 \cdot 10^{-6}$ [mol/dm^3].

The example of fluorescence emission quenching of the 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives by different concentrations of 4-(dimethylamino)benzoate (EDB) in acetonitrile.

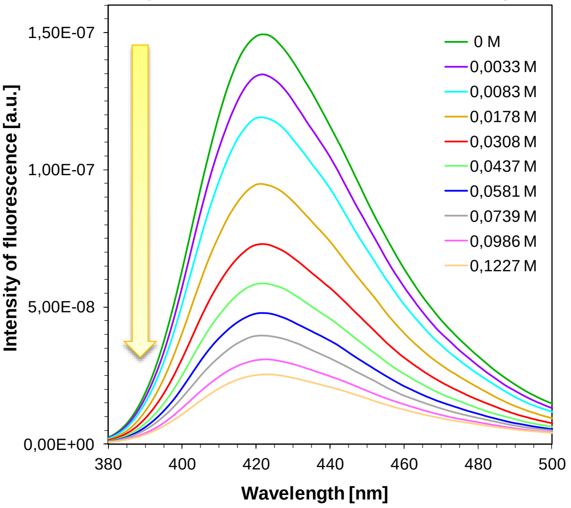


Fig. S41 Fluorescence emission quenching of S1 by different concentration of EDB in acetonitrile; concentration [S1]= 1,69·10^{-5} [mol/dm^3].

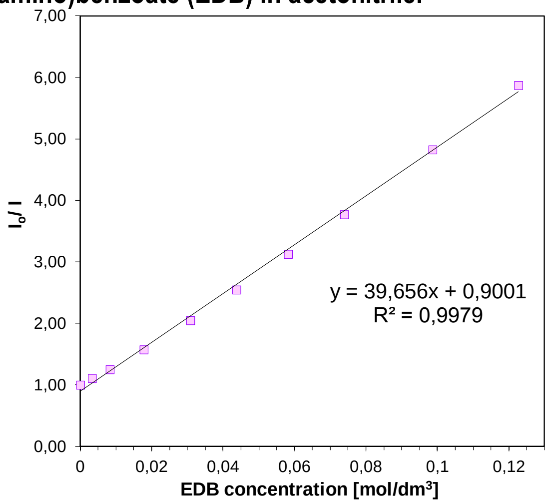


Fig. S42 Stern –Volmer plot for S1

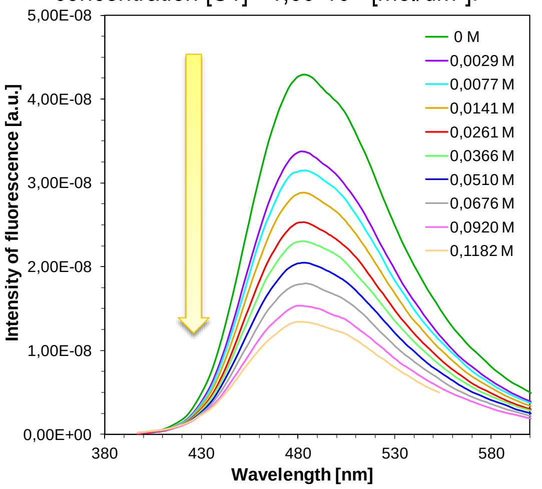


Fig. S43 Fluorescence emission quenching of S2 by different concentration of Speedcure 938 in acetonitrile; concentration [S2] = 4,04·10^{-5} [mol/dm^3].

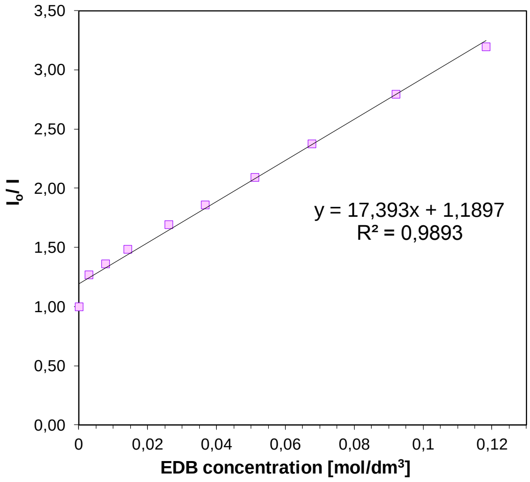


Fig. S44 Stern –Volmer plot for S2

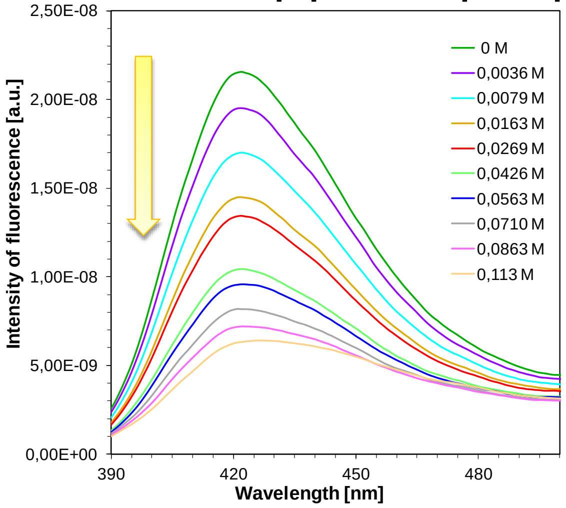


Fig. S45 Fluorescence emission quenching of S4 by different concentration of Speedcure 938 in acetonitrile; concentration [S4] = 1,63·10^{-5} [mol/dm^3].

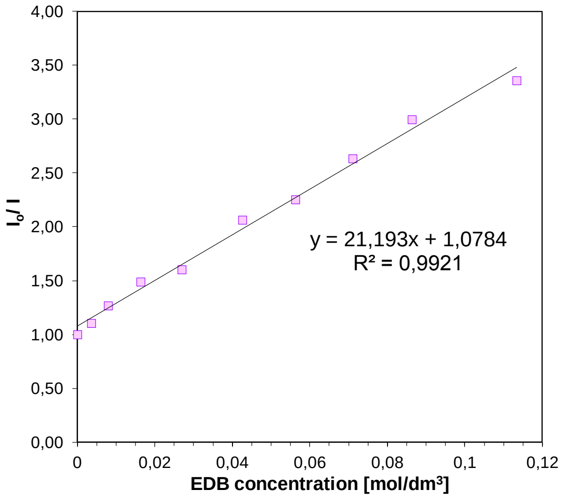


Fig. S46 Stern –Volmer plot for S4

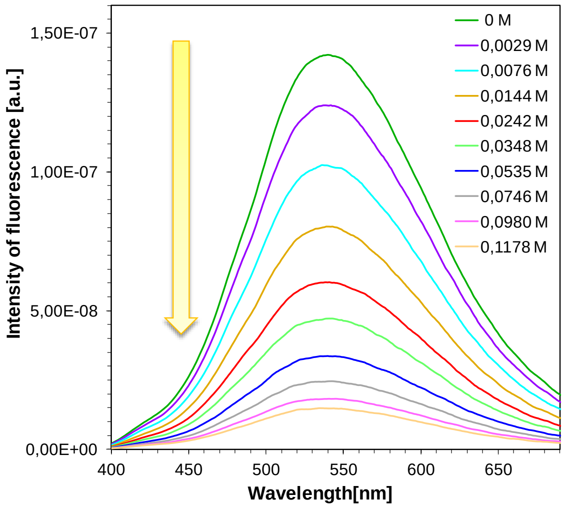


Fig. S47 Fluorescence emission quenching of S6 by different concentration of Speedcure 938 in acetonitrile; concentration [S6] = 1,02·10^{-5} [mol/dm^3].

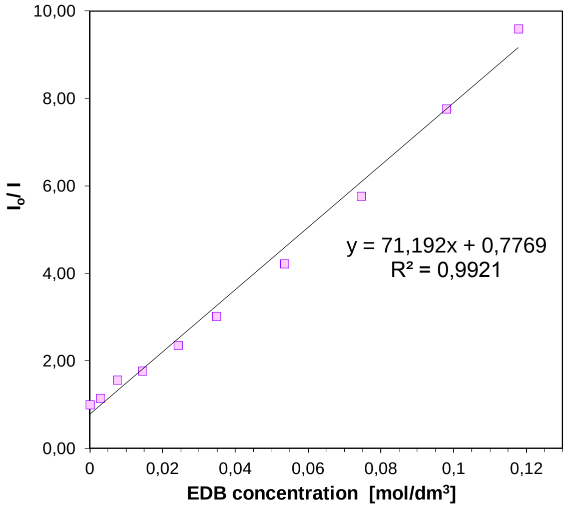


Fig. S48 Stern –Volmer plot for S6

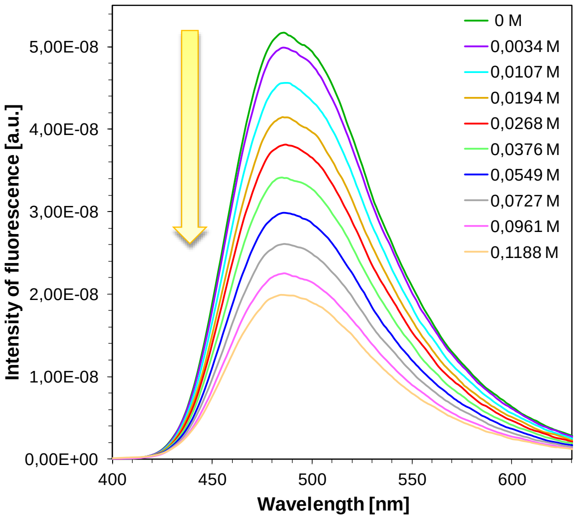


Fig. S49 Fluorescence emission quenching of S7 by different concentration of Speedcure 938 in acetonitrile; concentration [S7] = 2,30·10^{-5} [mol/dm^3].

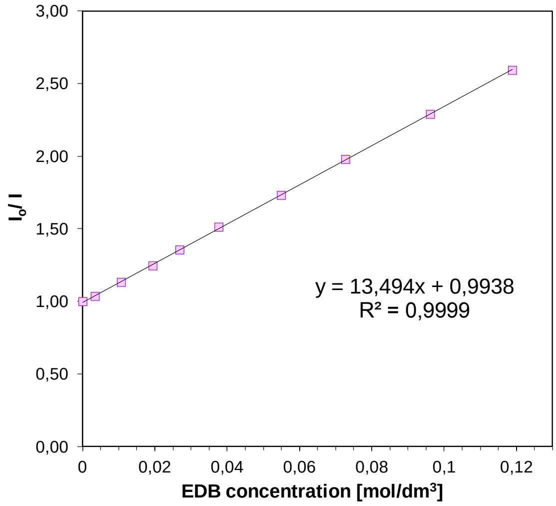


Fig. S50 Stern –Volmer plot for S7

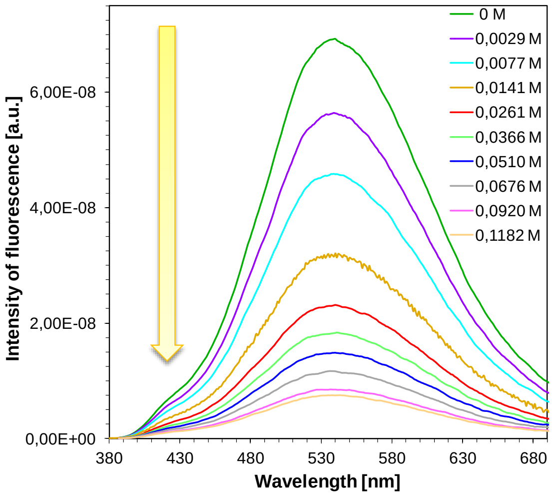


Fig. S51 Fluorescence emission quenching of S9 by different concentration of Speedcure 938 in acetonitrile; concentration [S9] = 1,53·10^{-5} [mol/dm^3].

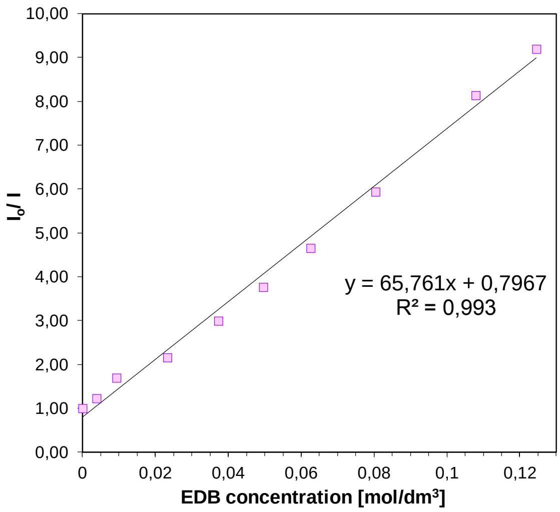


Fig. S52 Stern –Volmer plot for S9

Singlet state energy determination of the 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives in acetonitrile.

SERIES 1

SERIES 2

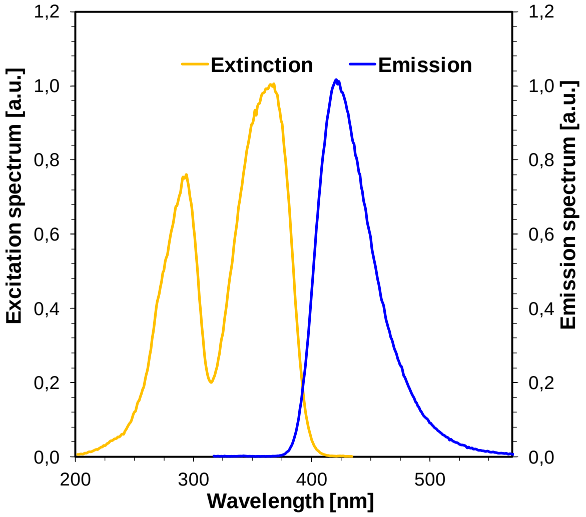


Fig. S53 Singlet state energy determination for S1 in acetonitrile.

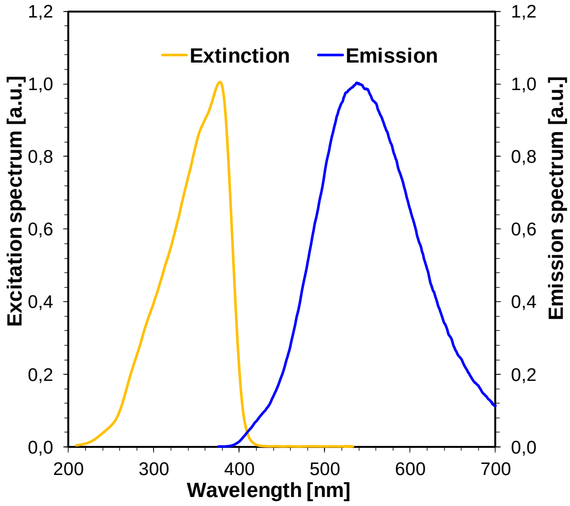


Fig. S54 Singlet state energy determination for S6 in acetonitrile.

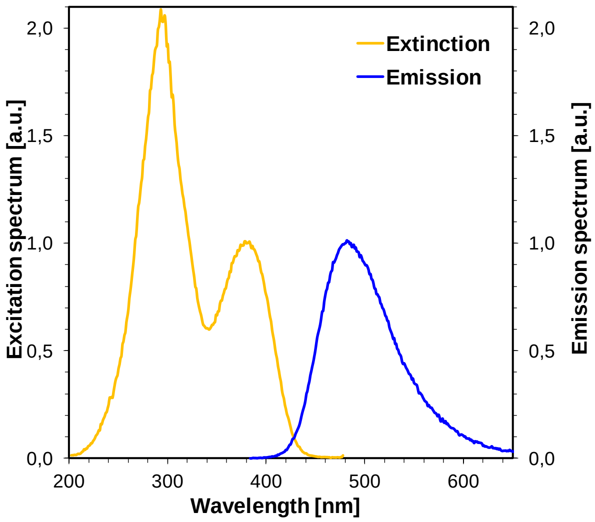


Fig. S55 Singlet state energy determination for S2 in acetonitrile.

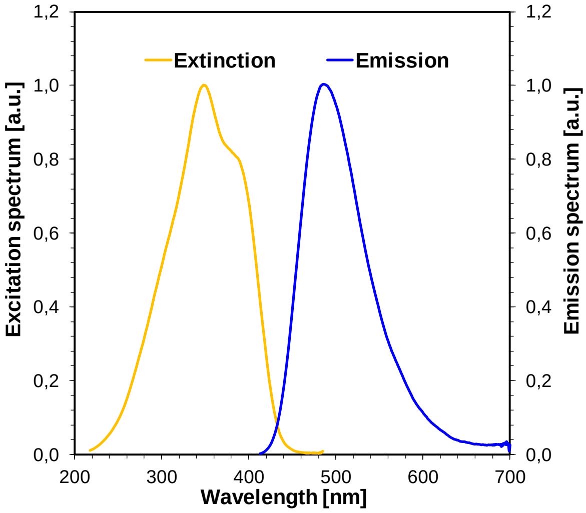


Fig. S56 Singlet state energy determination for S7 in acetonitrile.

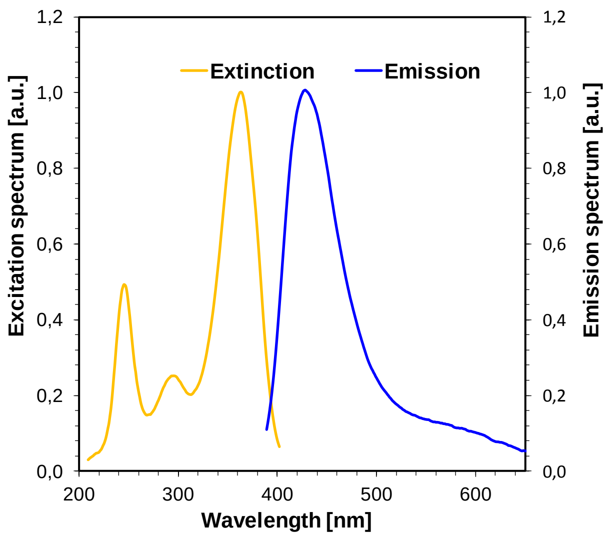


Fig. S57 Singlet state energy determination for S3 in acetonitrile.

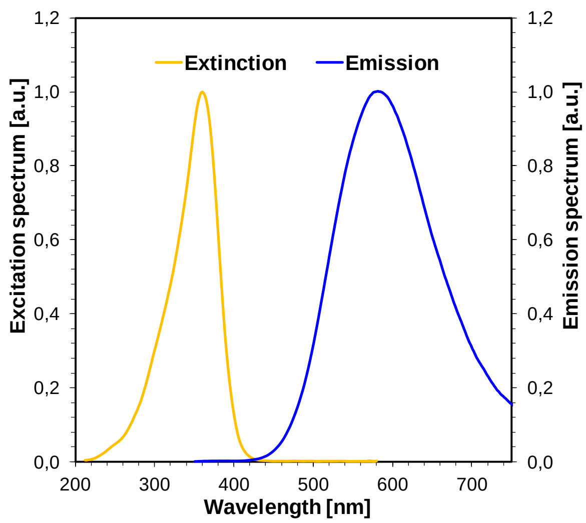


Fig. S58 Singlet state energy determination for S8 in acetonitrile.

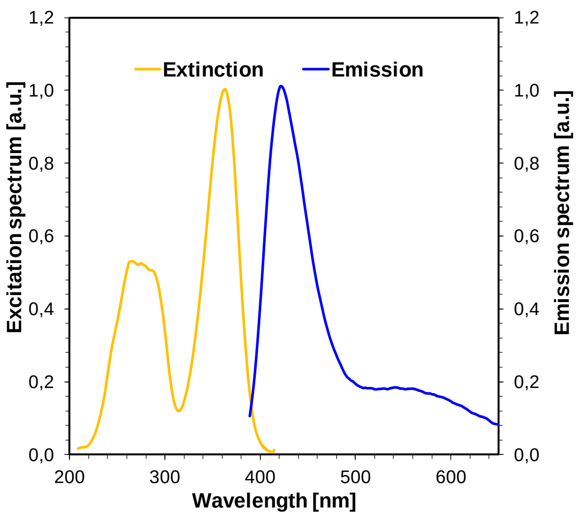


Fig. S59 Singlet state energy determination for S4 in acetonitrile.

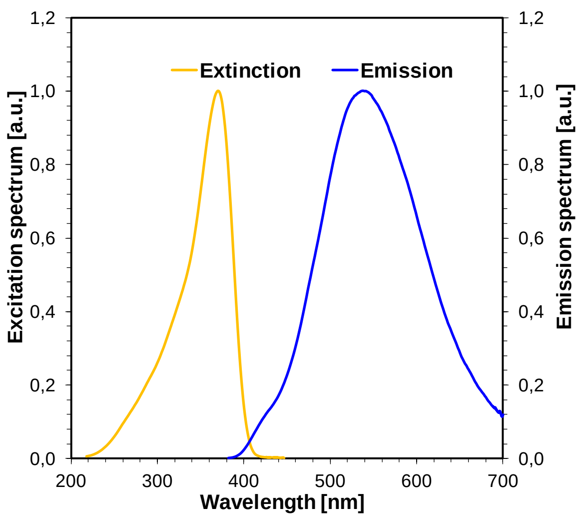


Fig. S60 Singlet state energy determination for S9 in acetonitrile.

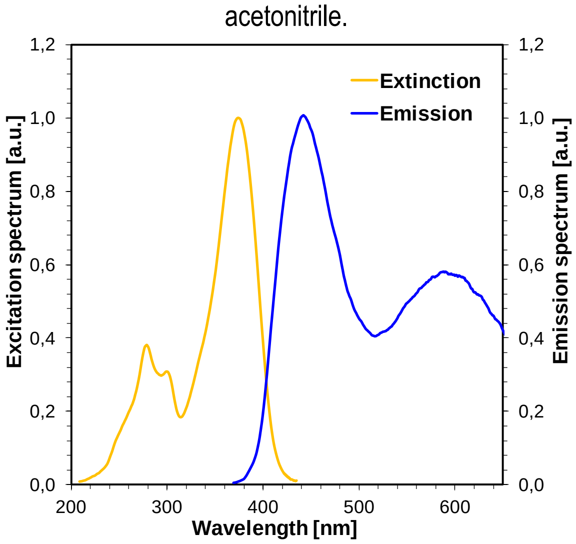


Fig. S61 Singlet state energy determination for S5 in acetonitrile.

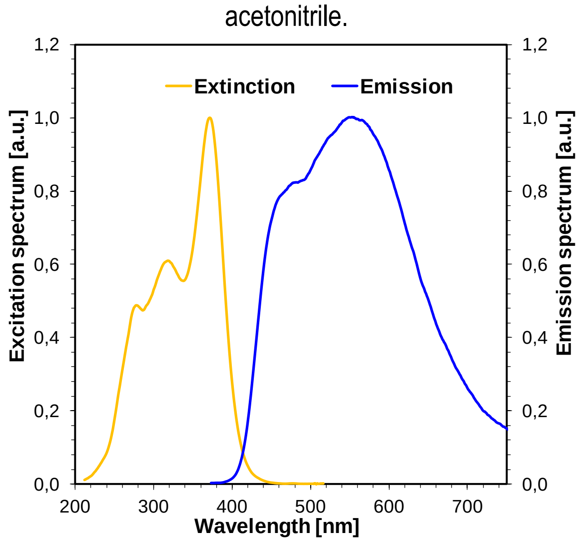


Fig. S62 Singlet state energy determination for S10 in acetonitrile.

Cyclic voltammetry curves showing oxidation and reduction processes of the 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives in acetonitrile.

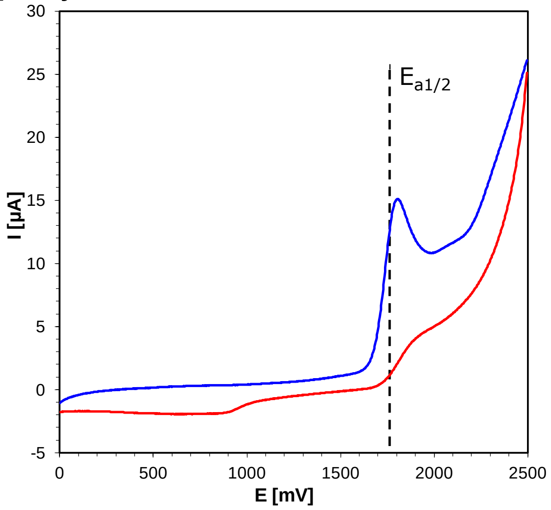


Fig. S63 Cyclic voltammogram curves of the S1 oxidation in acetonitrile.

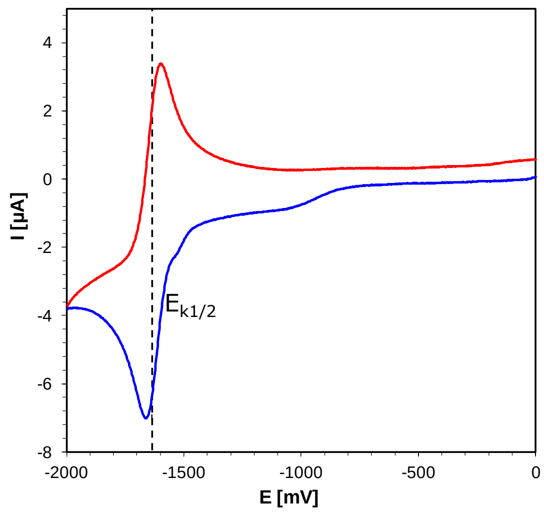


Fig. S64 Cyclic voltammogram curves of the S1 reduction in acetonitrile.

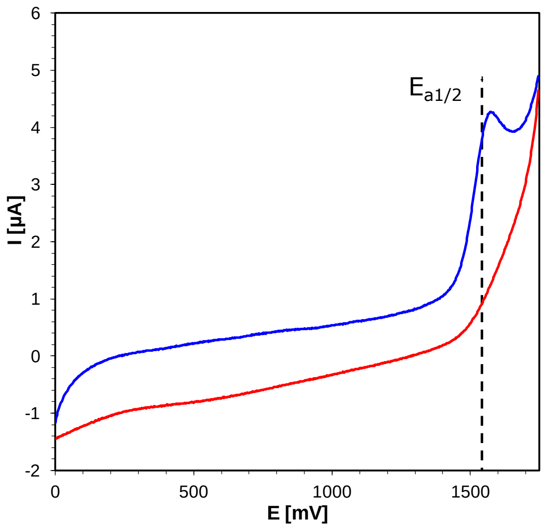


Fig. S65 Cyclic voltammogram curves of the S2 oxidation in acetonitrile.

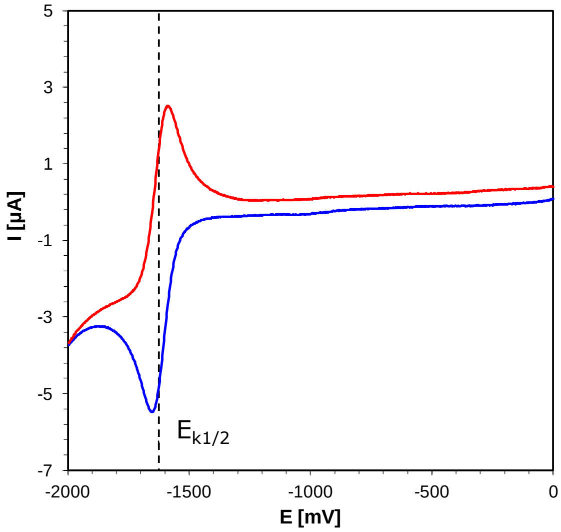


Fig. S66 Cyclic voltammogram curves of the S2 reduction in acetonitrile.

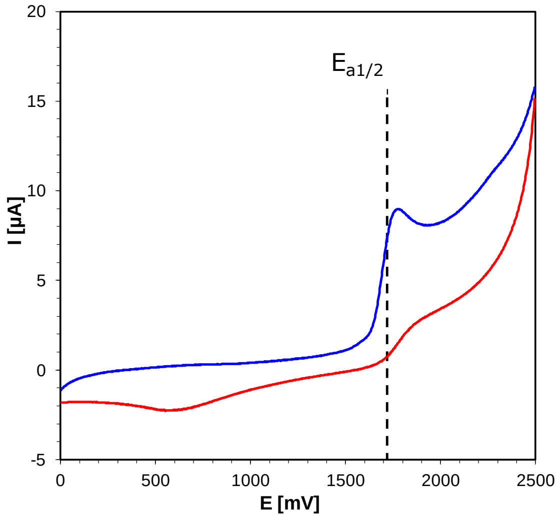


Fig. S67 Cyclic voltammogram curves of the S3 oxidation in acetonitrile.

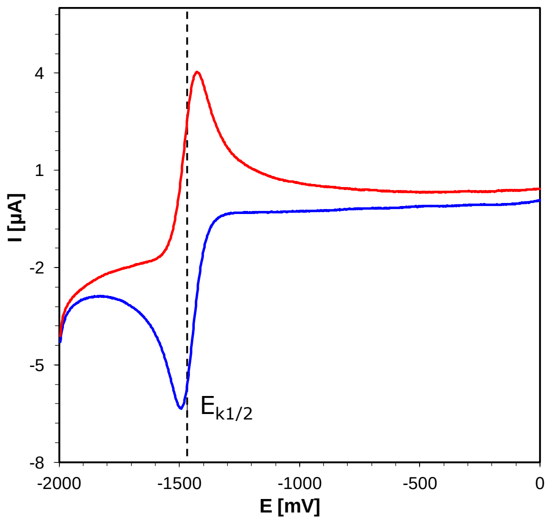


Fig. S68 Cyclic voltammogram curves of the S3 reduction in acetonitrile.

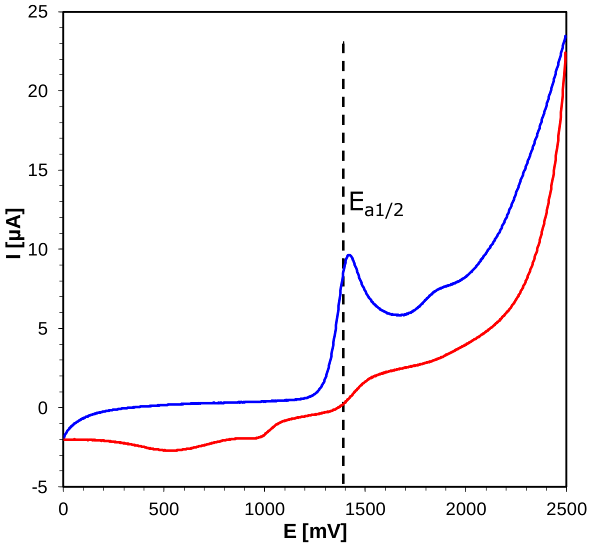


Fig. S69 Cyclic voltammogram curves of the S4 oxidation in acetonitrile.

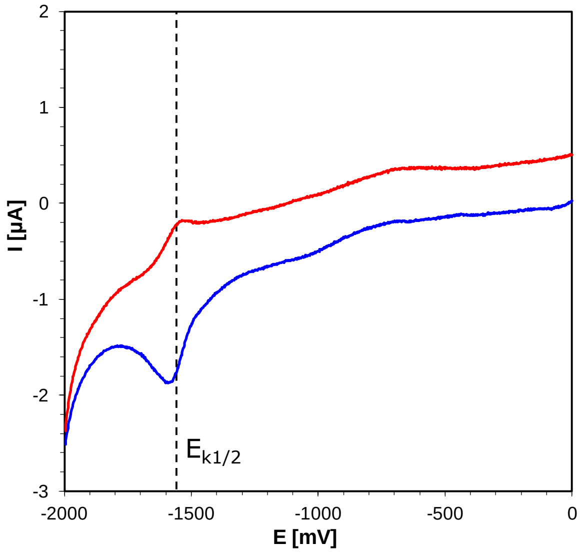


Fig. S70 Cyclic voltammogram curves of the S4 reduction in acetonitrile.

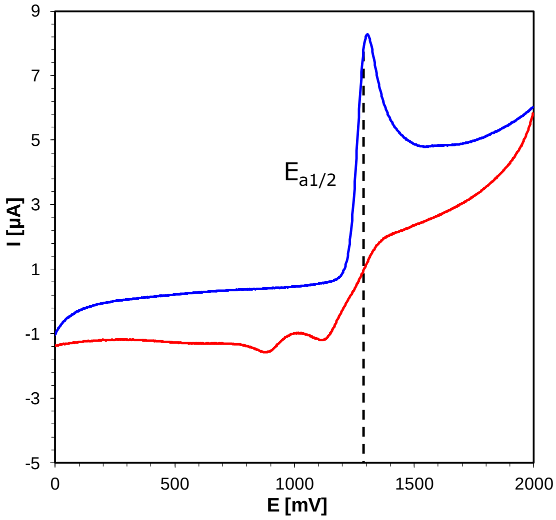


Fig. S71 Cyclic voltammogram curves of the S5 oxidation in acetonitrile.

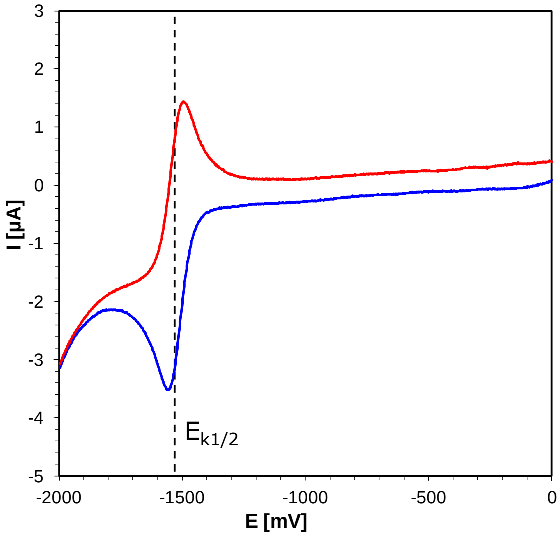


Fig. S72 Cyclic voltammogram curves of the S5 reduction in acetonitrile.

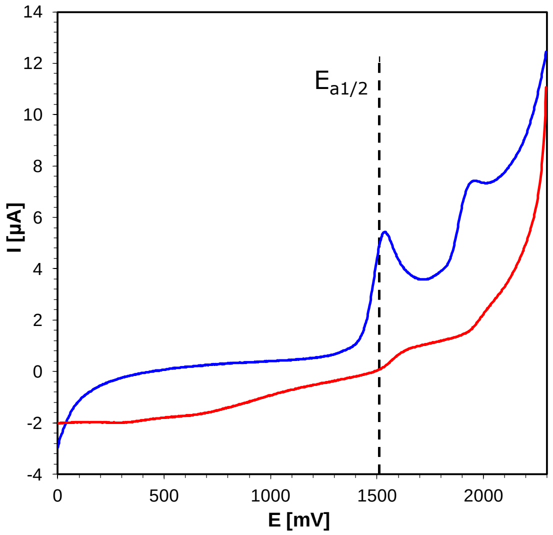


Fig. S73 Cyclic voltammogram curves of the S6 oxidation in acetonitrile.

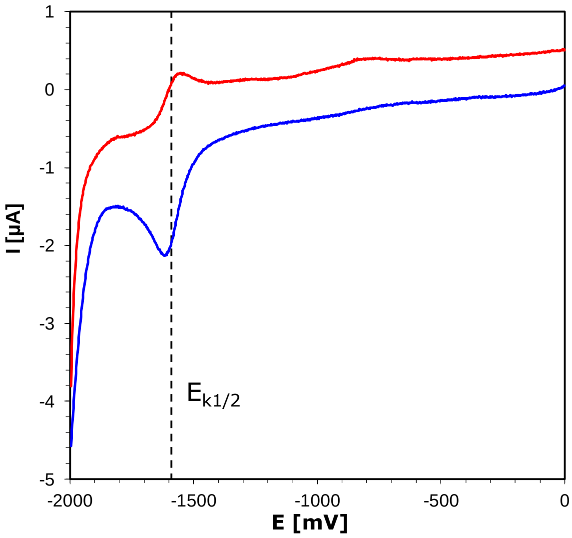


Fig. S74 Cyclic voltammogram curves of the S6 reduction in acetonitrile.

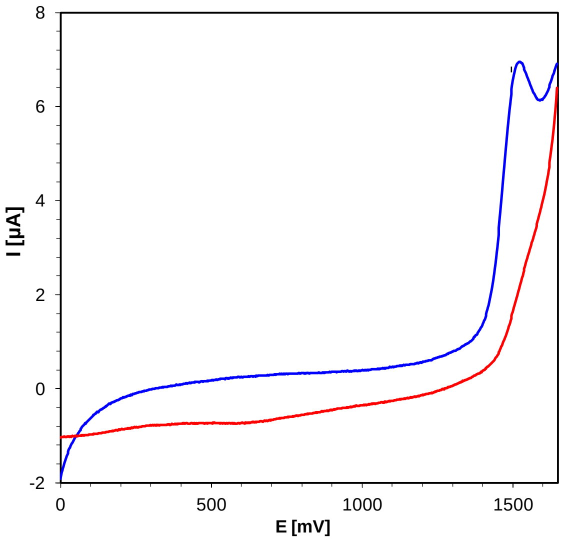


Fig. S75 Cyclic voltammogram curves of the S7 oxidation in acetonitrile.

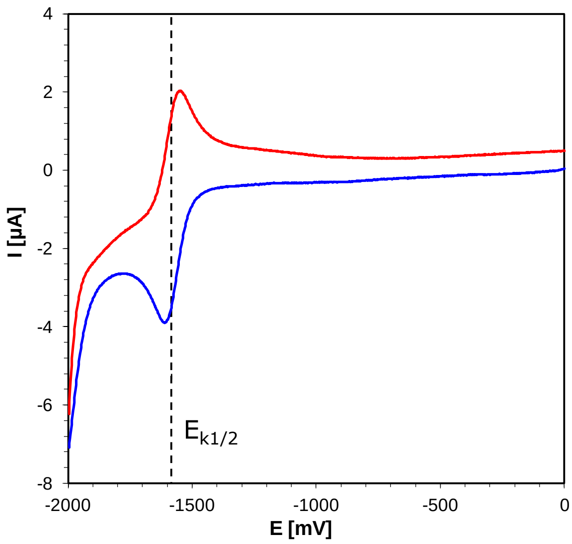


Fig. S76 Cyclic voltammogram curves of the S7 reduction in acetonitrile.

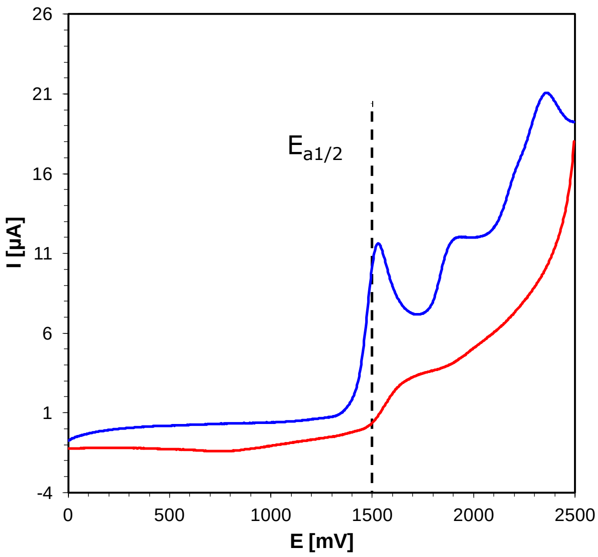


Fig. S77Cyclic voltammogram curves of the S8 oxidation in acetonitrile.

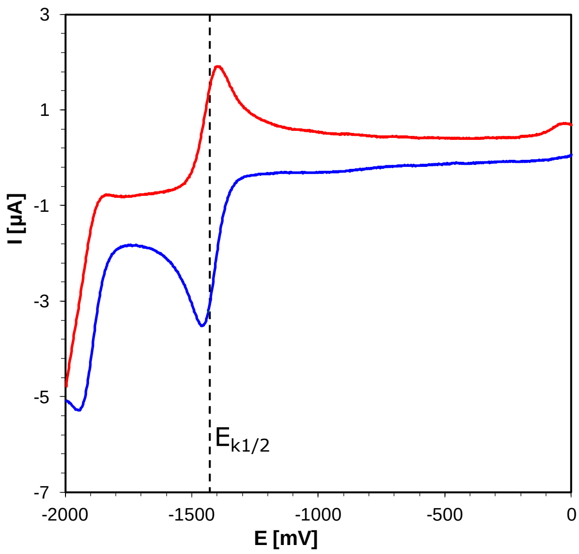


Fig. S78 Cyclic voltammogram curves of the S8 reduction in acetonitrile.

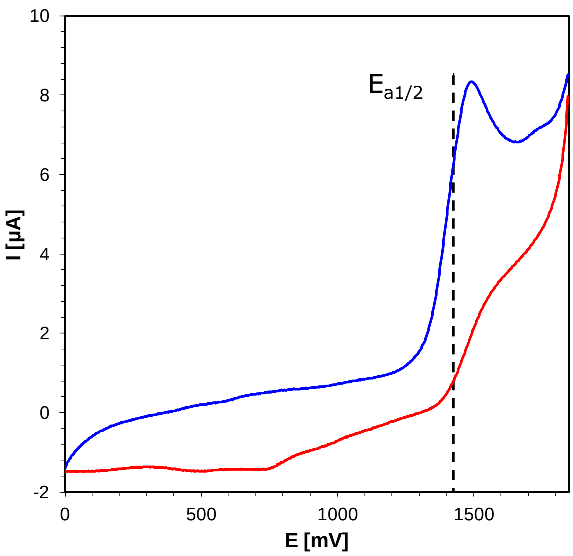


Fig. S79 Cyclic voltammogram curves of the S9 oxidation in acetonitrile.

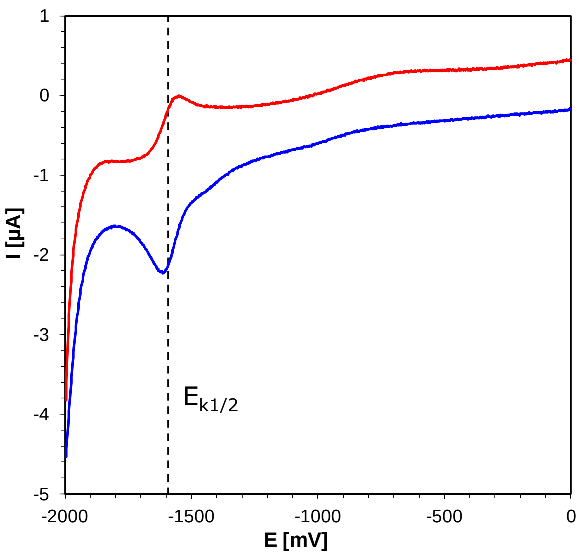


Fig. 80 Cyclic voltammogram curves of the S9 reduction in acetonitrile.

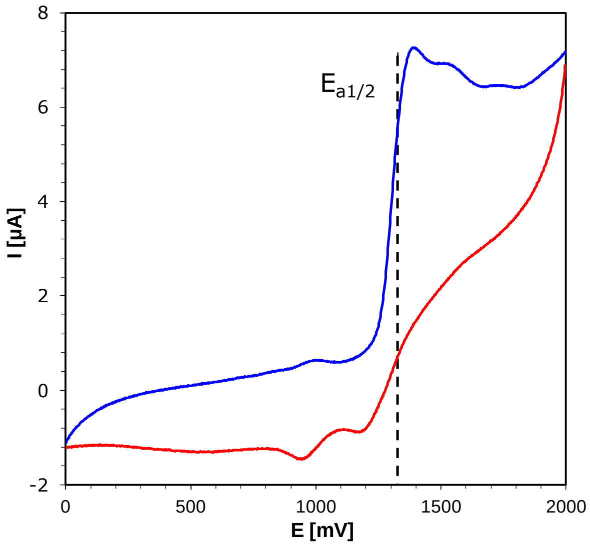


Fig. S81 Cyclic voltammogram curves of the S10 oxidation in acetonitrile.

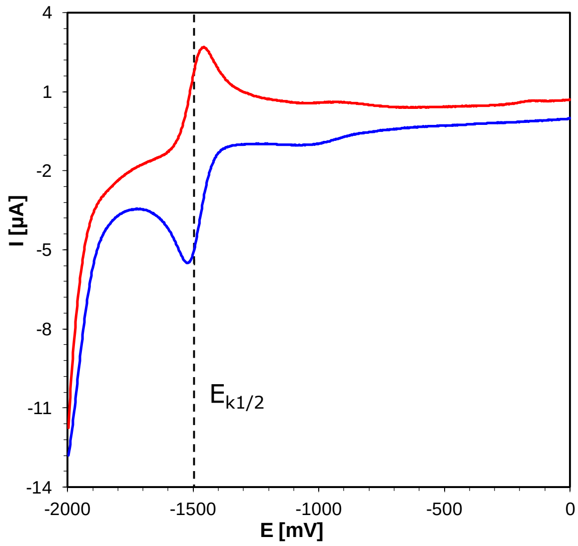
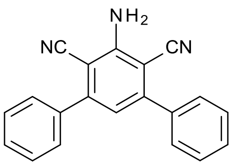
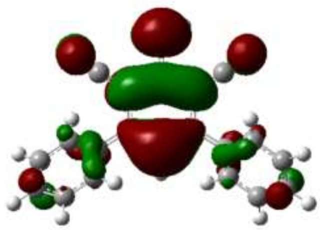
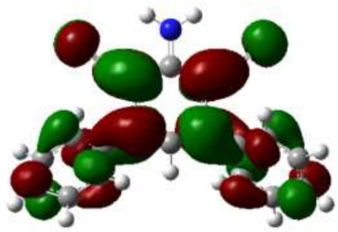
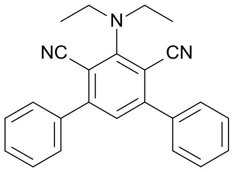
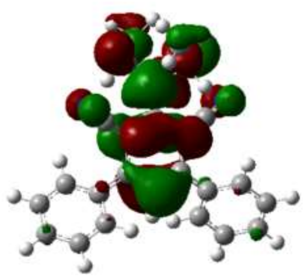
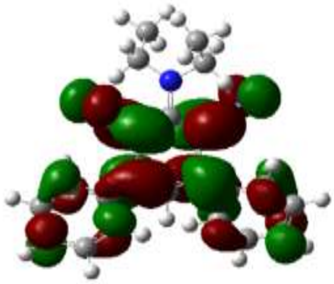
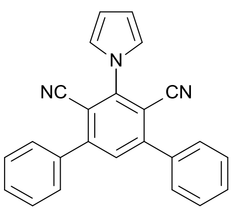
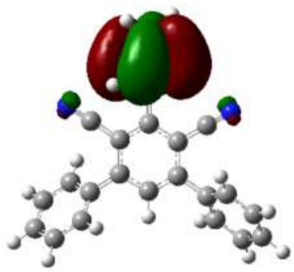
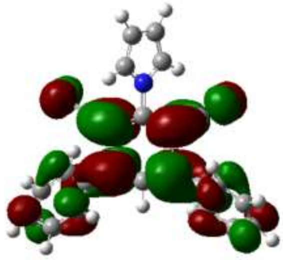
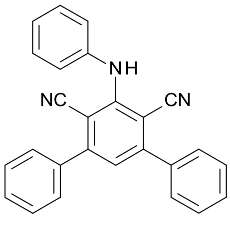
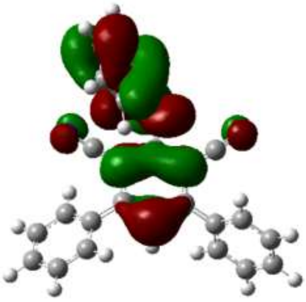
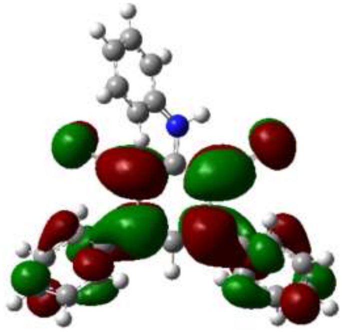
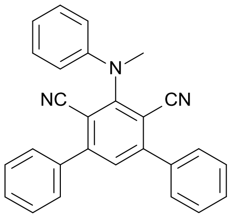
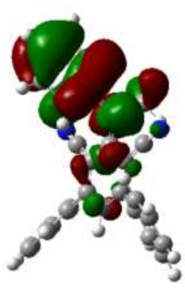
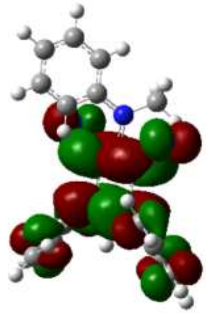
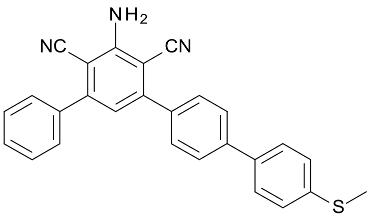
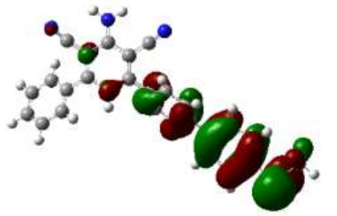
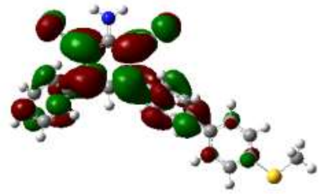
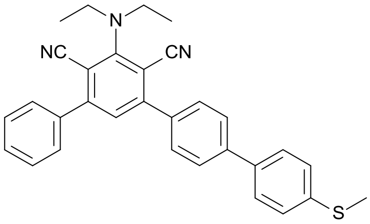
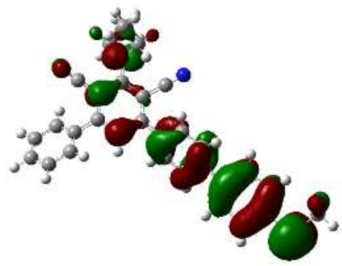
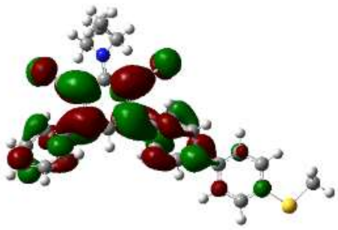
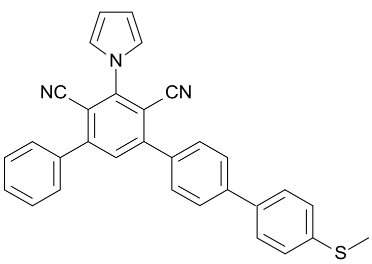
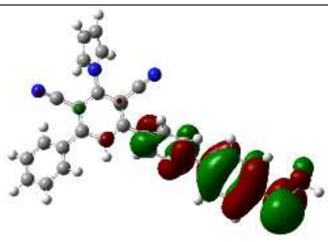
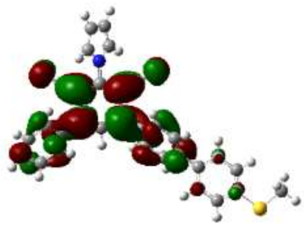
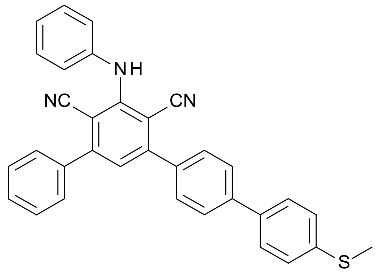
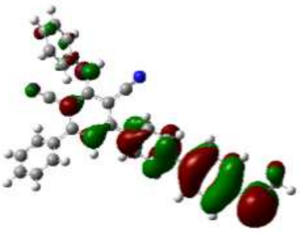
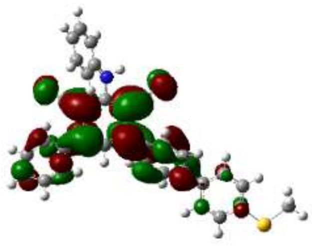
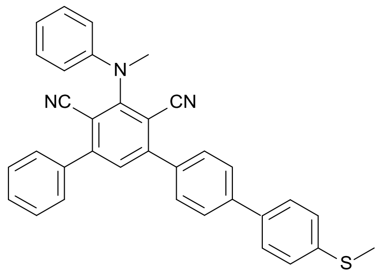
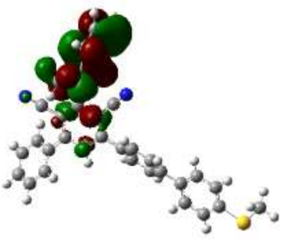
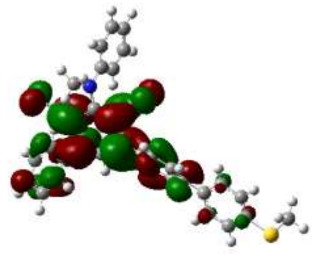


Fig. S82 Cyclic voltammogram curves of the S10 reduction in acetonitrile.

Contour plots of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives structures optimized at the B3LYP/6-31G* level of theory.

Compound	HOMO	LUMO
 **S1** **2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile**		
 **S2** **2-(diethylamino)-4,6-diphenyl-benzene-1,3-dicarbonitrile**		
 **S3** **4,6-diphenyl-2-pyrrol-1-yl-benzene-1,3-dicarbonitrile**		

 **S4** **2-anilino-4,6-diphenyl-benzene-1,3-dicarbonitrile**		
 **S5** **2-(N-methylanilino)-4,6-diphenyl-benzene-1,3-dicarbonitrile**		
 **S6** **2-amino-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile**		
 **S7** **2-(diethylamino)-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile**		
 **S8** **4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-2-pyrrol-1-yl-benzene-**		

1,3-dicarbonitrile		
 **S9** **2-anilino-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile**		
 **S10** **2-(N-methylanilino)-4-[4-(4-thiomethylphenyl)phenyl]-6-phenyl-benzene-1,3-dicarbonitrile**		

Photopolymerization profiles of UviCure S105 upon exposure to LED@365 and LED420nm under air in the presence of different photoinitiating systems based on Speedcure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 1 and 2.

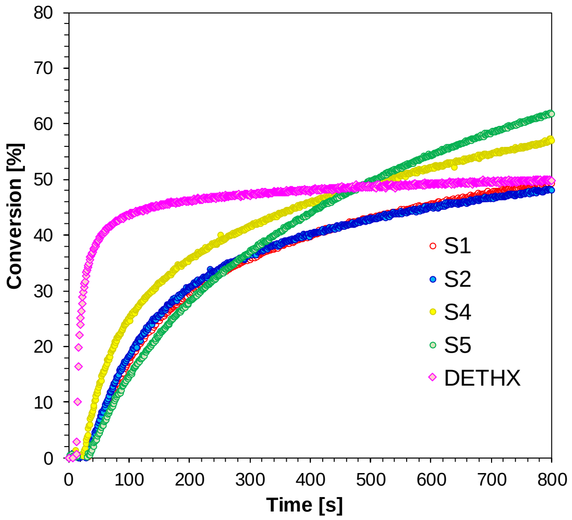


Fig. S83 Photopolymerization profiles of UviCure S105 (epoxy function conversion vs. irradiation time) upon exposure to the LED@365 nm under air in the presence of different photoinitiating systems based on Speedcure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 1. The irradiation starts at t = 10 s.

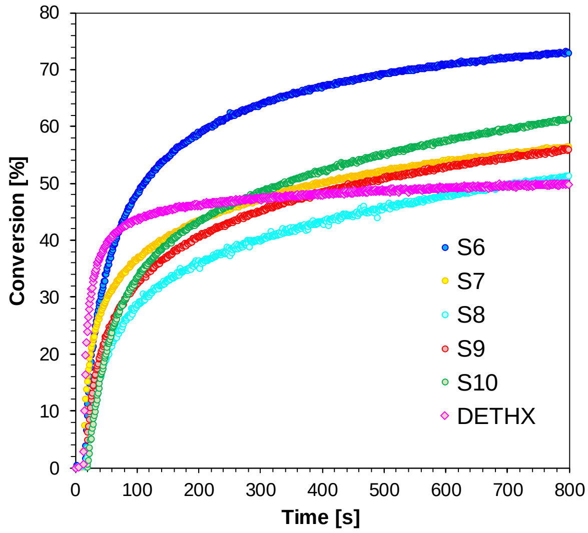


Fig. S84 Polymerization profiles of UviCure S105 (epoxy function conversion vs. irradiation time) upon exposure to the LED@365 nm under air in the presence of different photoinitiating systems based on Speedcure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 2. The irradiation starts at t = 10 s.

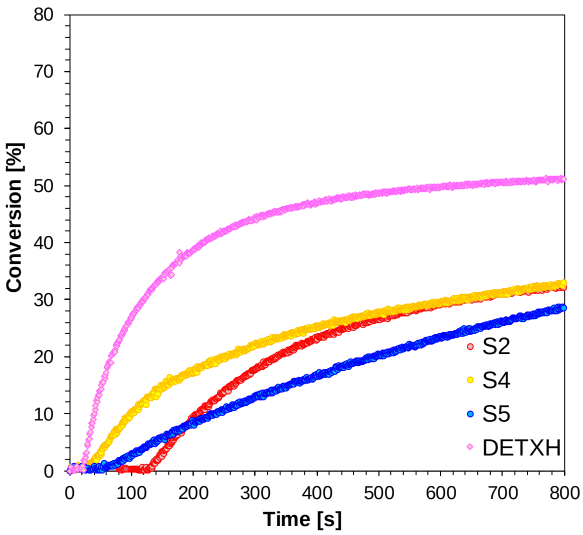


Fig. S85 Polymerization profiles of UviCure S105 (epoxy function conversion vs. irradiation time) upon exposure to the LED@420 nm under air in the presence of different photoinitiating systems based on SpeedCure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 1. The irradiation starts at t = 10 s.

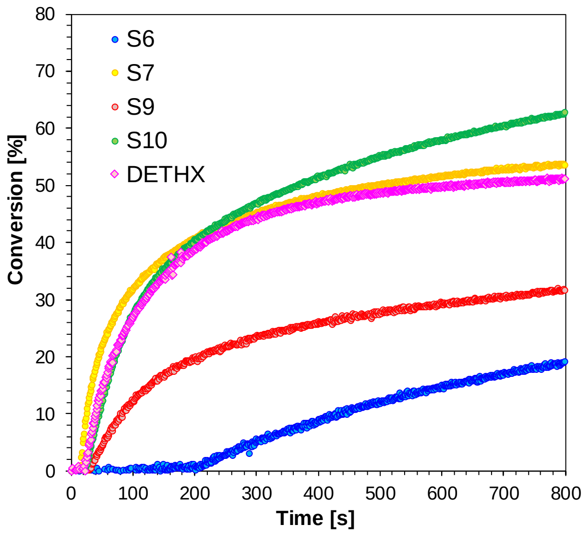


Fig. S86 Polymerization profiles of UviCure S105 (epoxy function conversion vs. irradiation time) upon exposure to the LED@420 nm under air in the presence of different photoinitiating systems based on SpeedCure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 2. The irradiation starts at t = 10 s.

Photopolymerization profiles of TMPTA upon exposure to LED@365 and LED420nm in the presence of different photoinitiating systems based on Speedcure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 1 and 2.

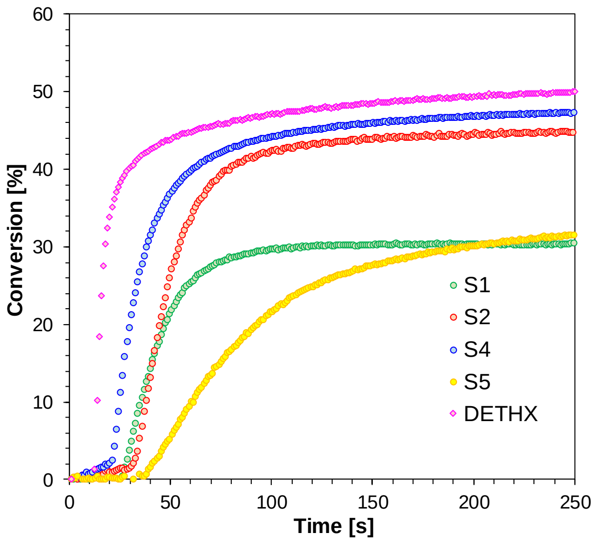


Fig. S87 Photopolymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) upon exposure to the LED@365 nm in laminate in the presence of different photoinitiating systems based on Speedcure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 1. The irradiation starts at t = 10 s.

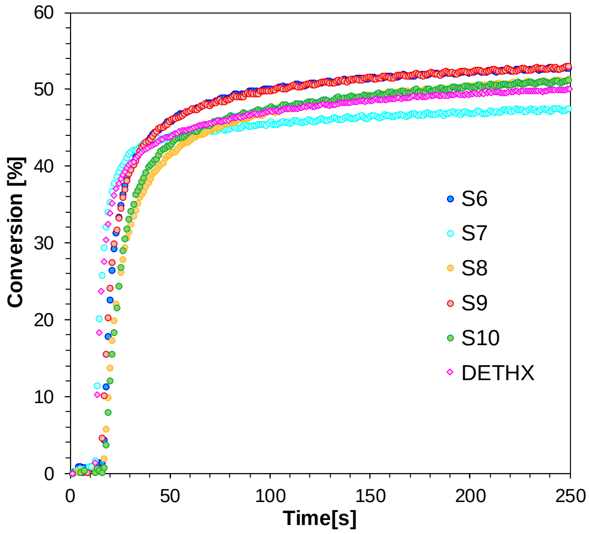


Fig. S88 Photopolymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) upon exposure to the LED@365 nm in laminate in the presence of different photoinitiating systems based on SpeedCure 938 (1% w/w) and 2-amino 4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 2. The irradiation starts at t = 10 s

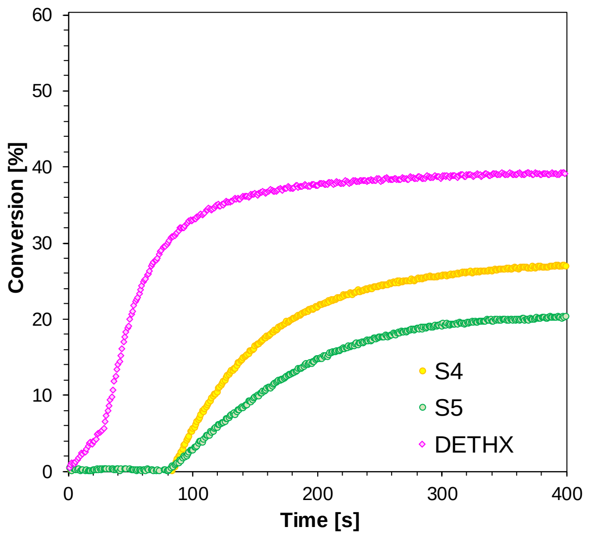


Fig. S89 Polymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) upon exposure to the LED@420 nm in laminate in the presence of different photoinitiating systems based on SpeedCure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 1. The irradiation starts at t = 10 s.

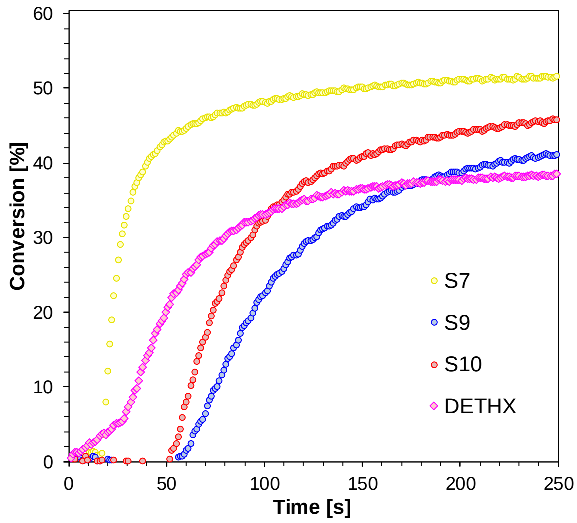


Fig. S90 Polymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) upon exposure to the LED@420 nm in laminate in the presence of different photoinitiating systems based on SpeedCure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 2. The irradiation starts at t = 10 s.

FT-IR spectra before and after photopolymerization processes of UviCure S105, TMPTA, TATATO/MERCAPTO (1:1) AND BisGMA/TEGDMA in the presence of different photoinitiating systems based on Speedcure 938 (1% w/w) and 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives from series 1 and 2 upon exposure to different LEDs

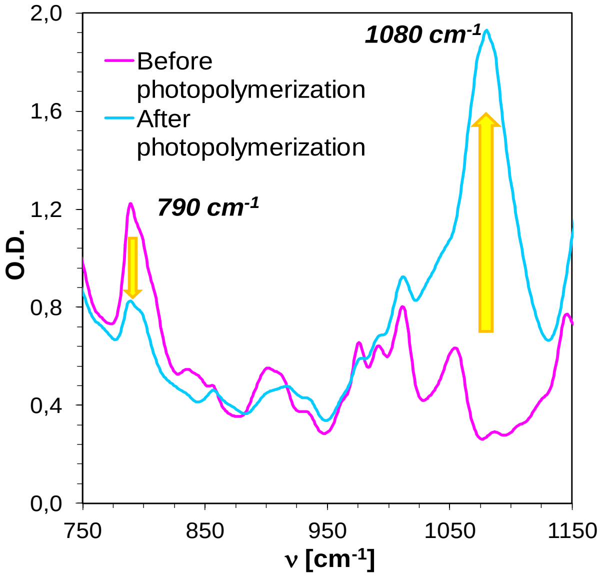


Fig. S91 FTIR spectra before and after photopolymerization of UviCure S105 monomer under LED@405 nm irradiation in composition with SpeedCure 938 (1% w/w) and S10.

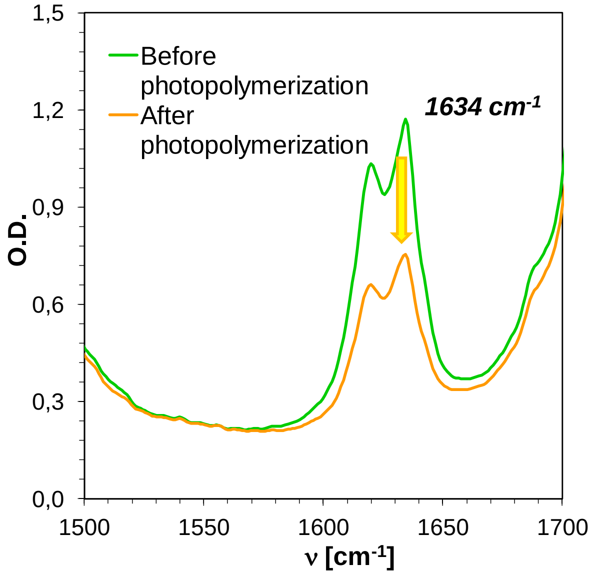


Fig. S92 FTIR spectra of double bonds band before and after photopolymerization of TMPTA under LED@365 irradiation in composition with SpeedCure 938 (1% w/w) and S4.

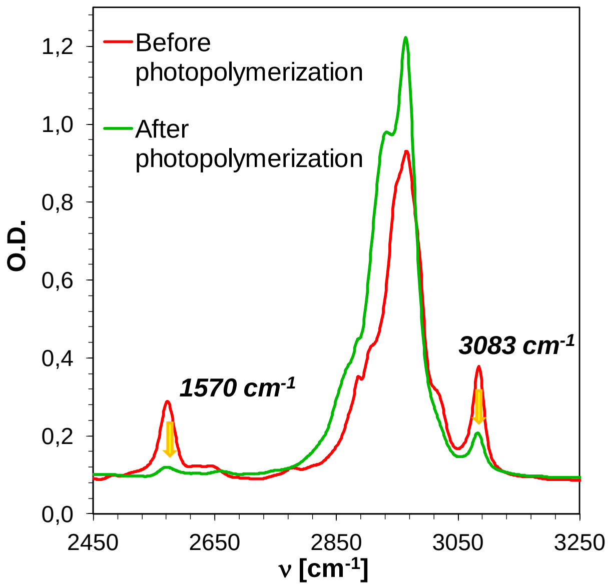


Fig. S93 FTIR spectra before and after photopolymerization of TATATO/MERCAPTO (1:1) monomers under LED@405 nm irradiation in composition with SpeedCure 938 (1% w/w) and S5.

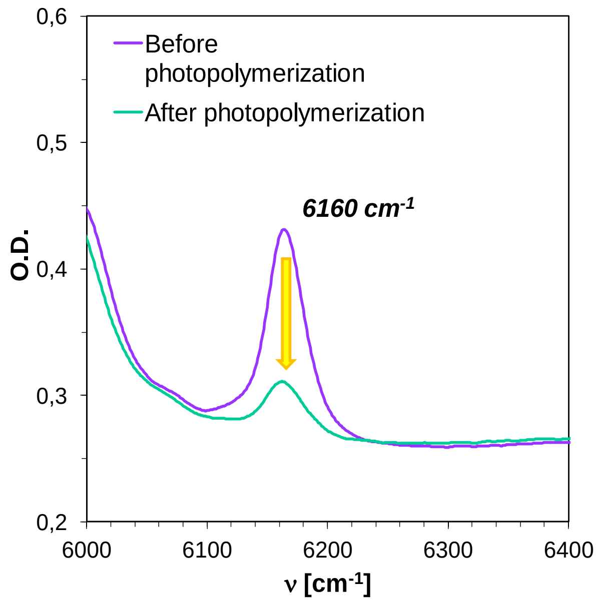


Fig. S94 FTIR spectra before and after photopolymerization of BisGMA/TEGDMA (7:3) monomers under LED@405 nm irradiation in composition with SpeedCure 938 (1% w/w) and S7.

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[1] J. Sepioł, P. Milart, *Tetrahedron*,1985, **41**, 5261-5265.
[2] J. Sepioł, P. Milart, *Tetrahedron Lett.*,1990, **31**, 2735-2738.