Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Novel photoinitiators based on difluoroborate complexes of squaraine dyes for radical polymerization of acrylates upon visible light

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1. Photodegradation - Steady state photolysis

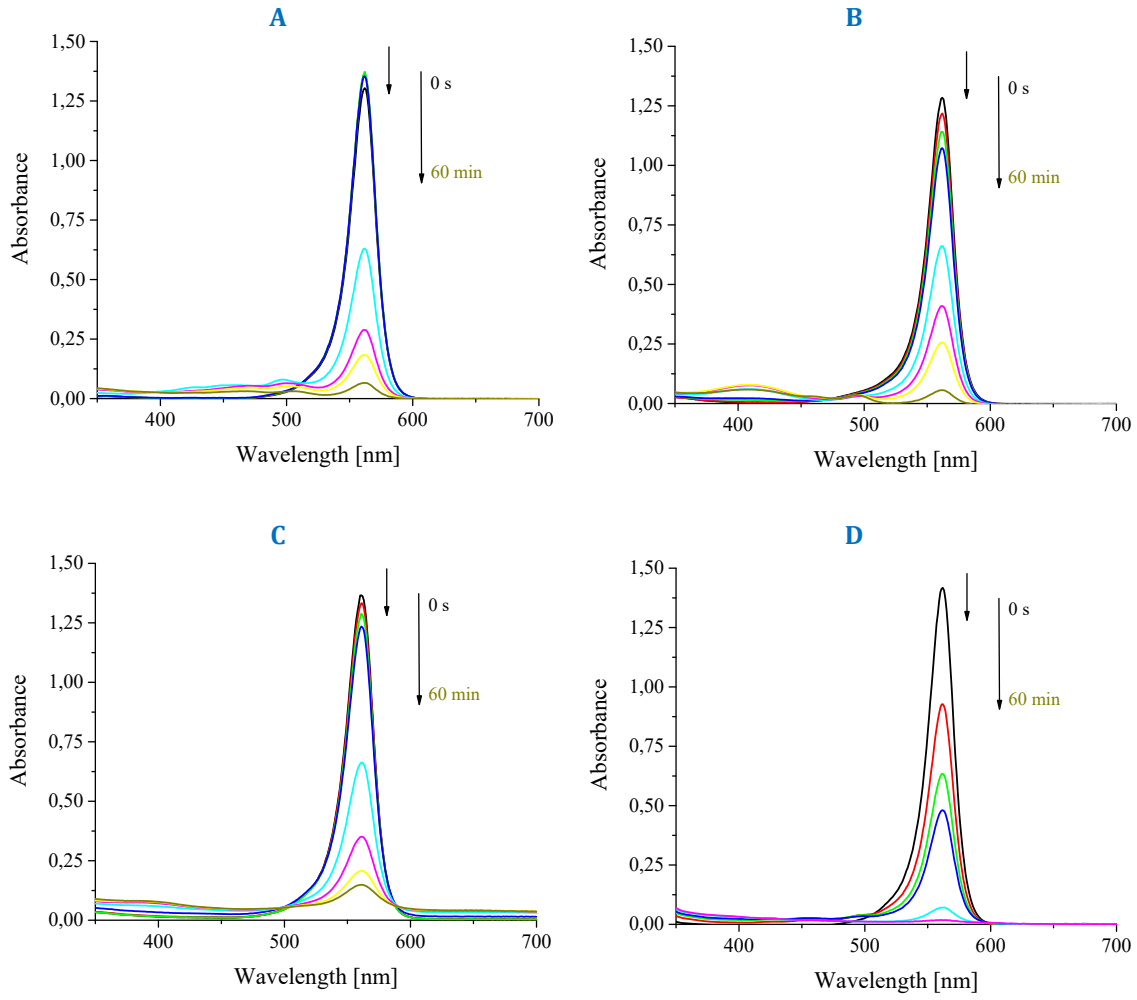
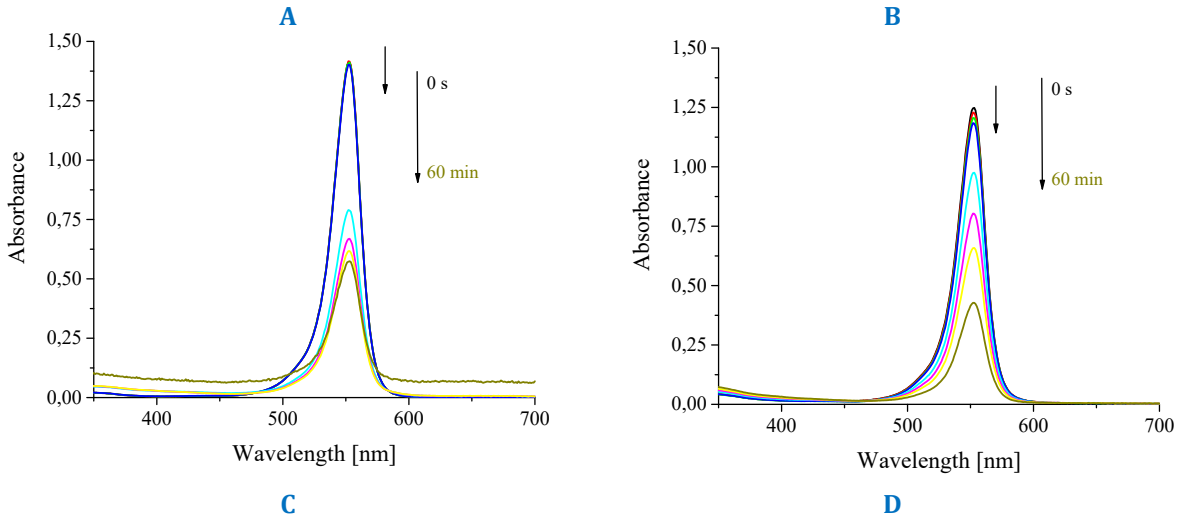


Figure S1. UV-Vis absorption spectra obtained upon photolysis of (A) PSQ2 alone, (B) PSQ2/B2, (C) PSQ2/I1 and (D) PSQ2/NO in acetonitrile upon irradiation at 518 nm (light intensity 50 mW cm^{-2}, co-initiator concentration 1 x 10^{-3} M)



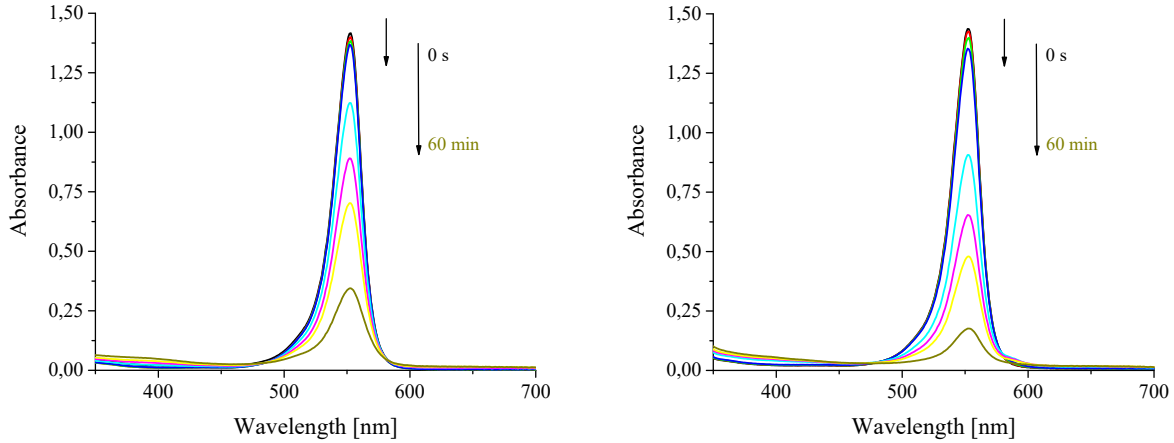


Figure S2 UV-Vis absorption spectra obtained upon photolysis of (A) BPSQ1 alone, (B) BPSQ1/B2, (C) BPSQ1/I1 and (D) BPSQ1/NO in acetonitrile upon irradiation at 518 nm (light intensity 50 mW cm^{-2}, co-initiator concentration 1 x 10^{-3} M)

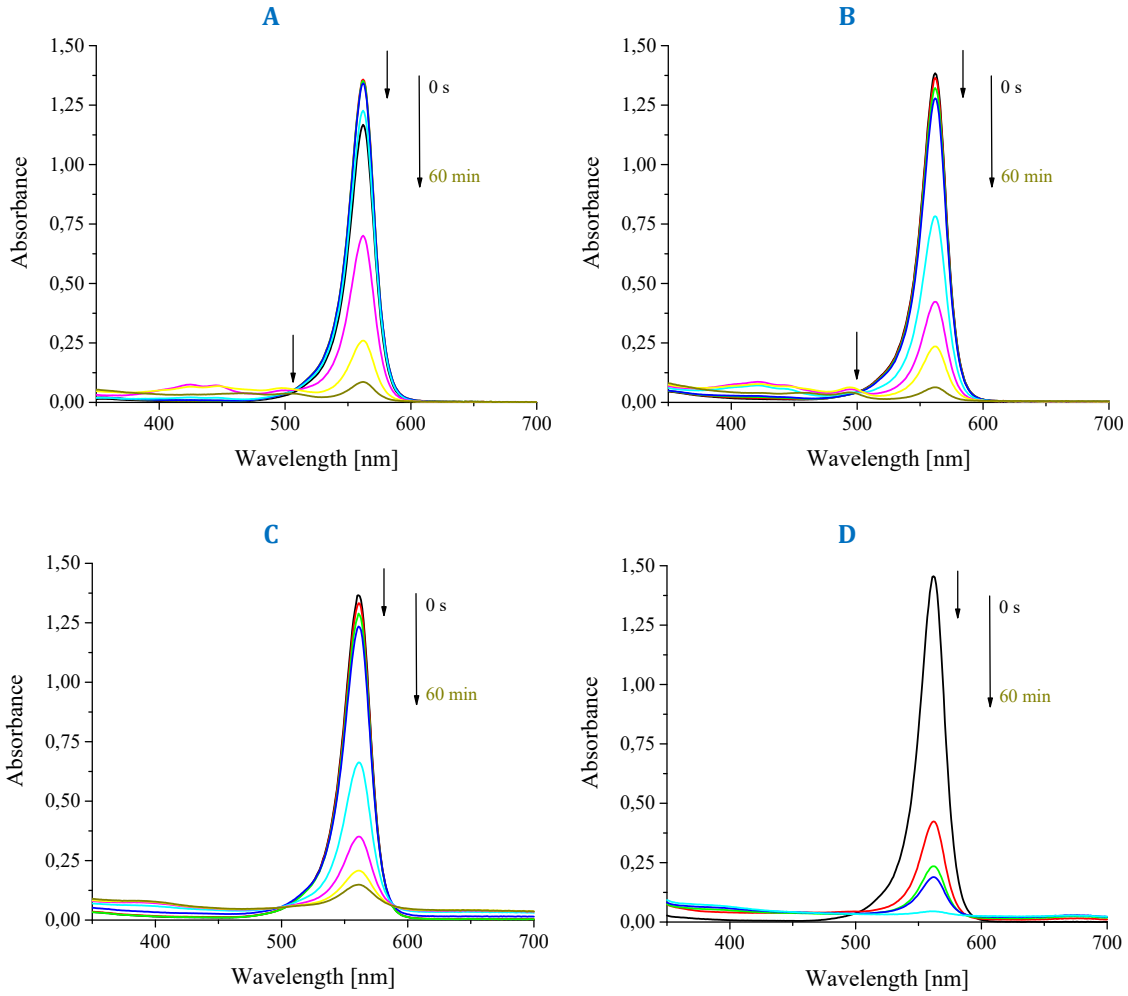


Figure S3 UV-Vis absorption spectra obtained upon photolysis of (A) BPSQ2 alone, (B) BPSQ2/B2, (C) BPSQ2/I1 and (D) BPSQ2/NO in acetonitrile upon irradiation at 518 nm (light intensity 50 mW cm^{-2}, co-initiator concentration 1 x 10^{-3} M)

2. ^{1}H NMR spectra

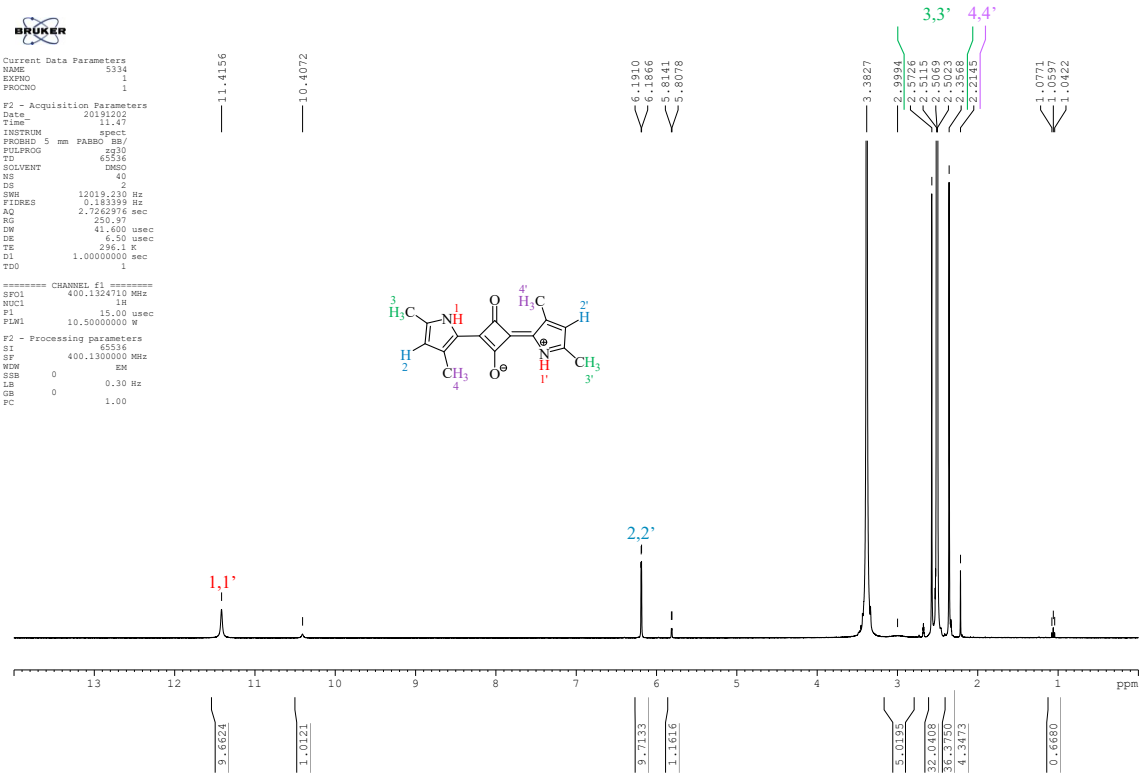


Figure S4 ^{1}H NMR spectra of 2,4-*bis*(3,5-dimethylpyrrol-2-yl)squaraine (PSQ1) recorded in DMSO-d_6

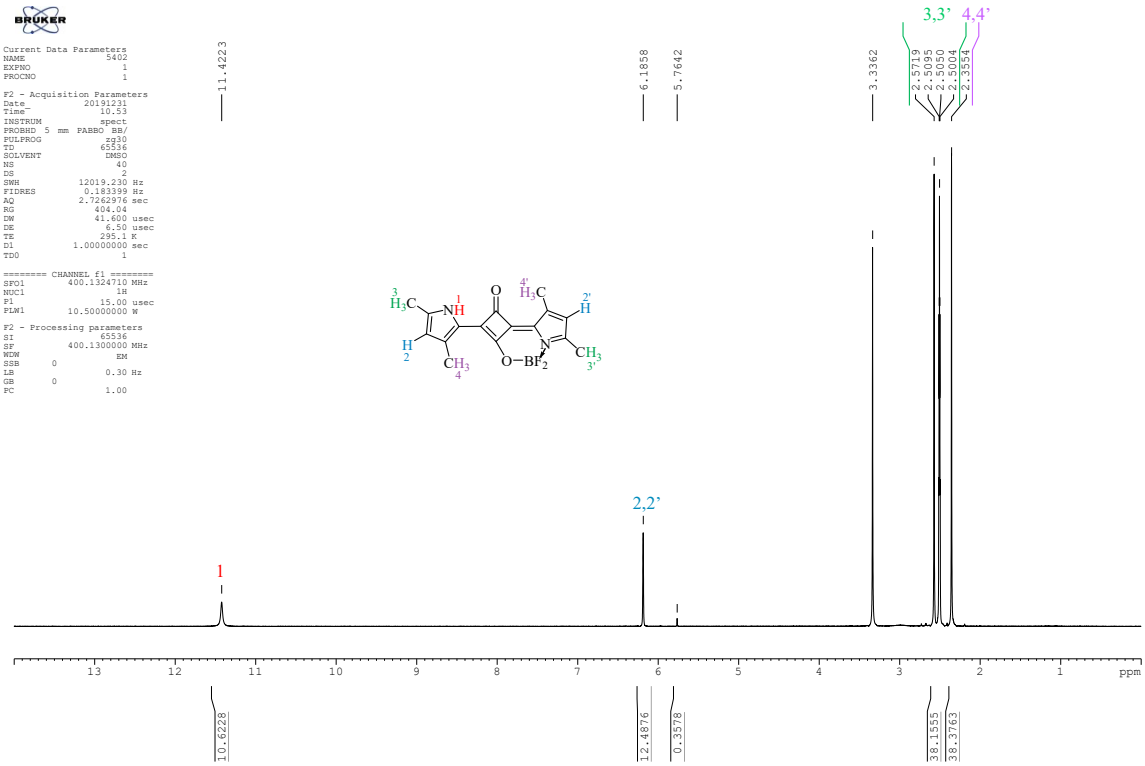


Figure S5 ^{1}H NMR spectra of 2,4-*bis*(3,5-dimethylpyrrol-2-yl)squaraine dichloroborate complex (BPSQ1) recorded in DMSO-d_6

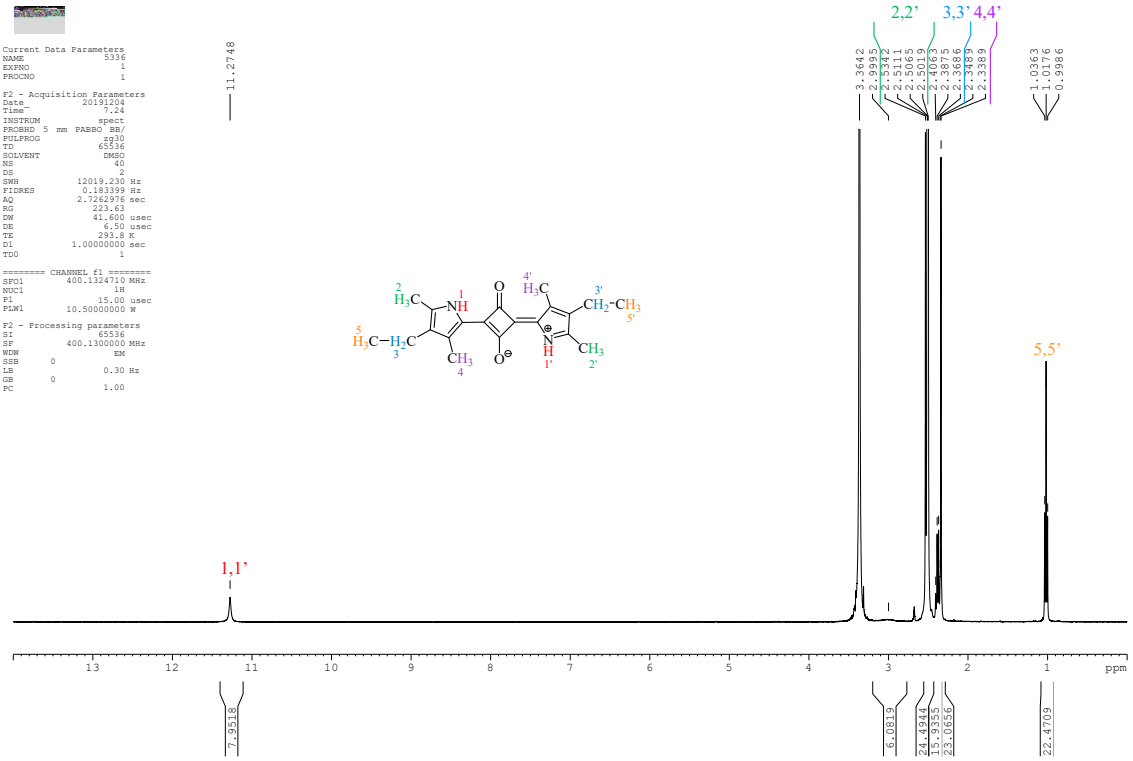


Figure S6 ^{1}H NMR spectra of 2,4-*bis*(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine (PSQ2) recorded in DMSO-d_6

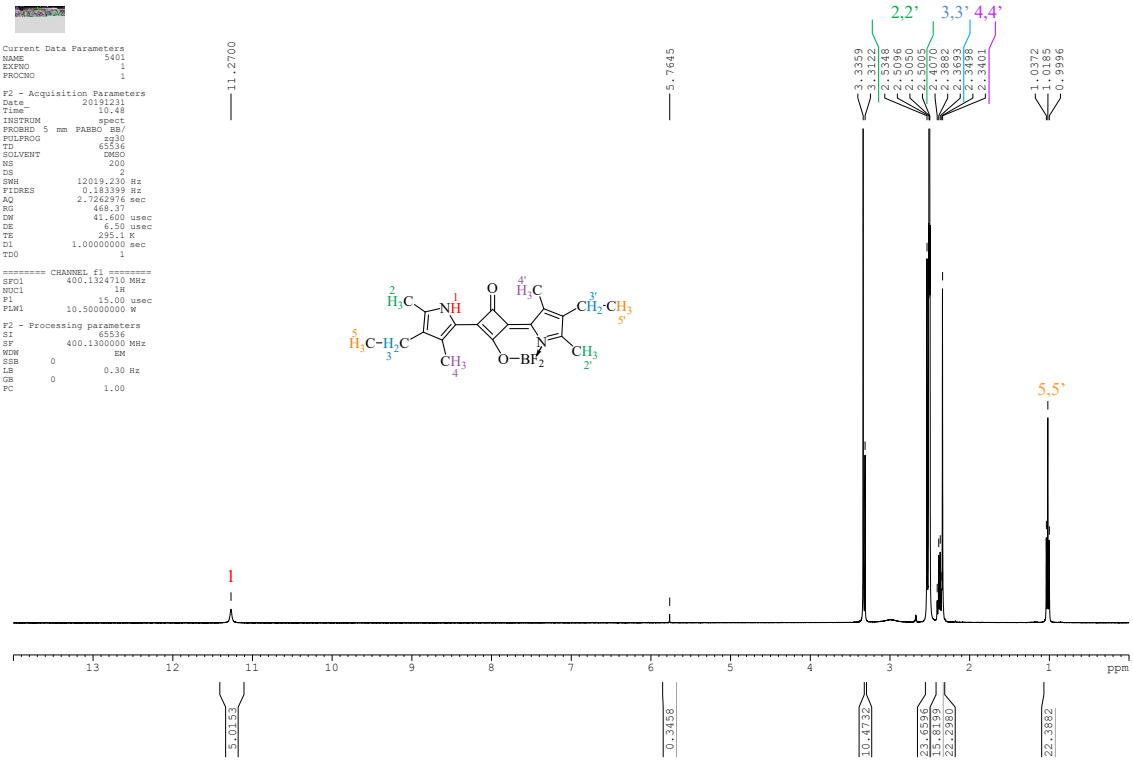


Figure S7 ^{1}H NMR spectra of 2,4-*bis*(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine (BPSQ2) difluoroborate complex recorded in DMSO-d_6

3. ^{13}C NMR spectra

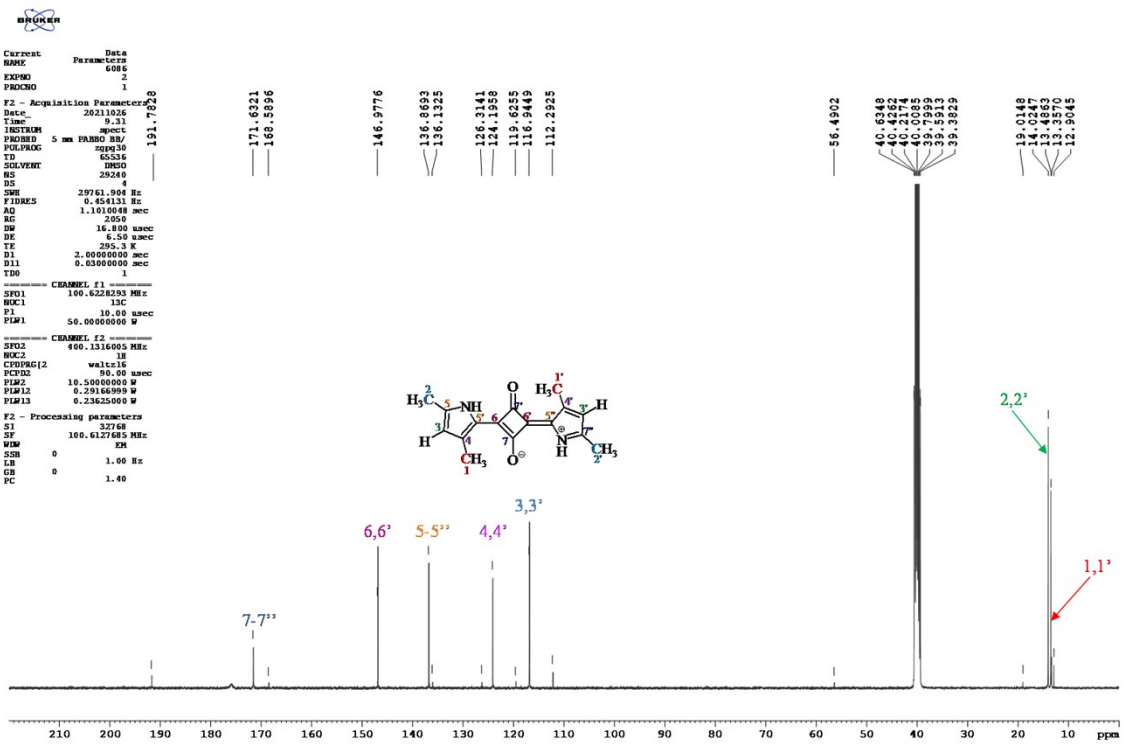


Figure S8 ^{13}C NMR spectra of 2,4-*bis*(3,5-dimethylpyrrol-2-yl)squaraine (PSQ1) recorded in DMSO-d_6

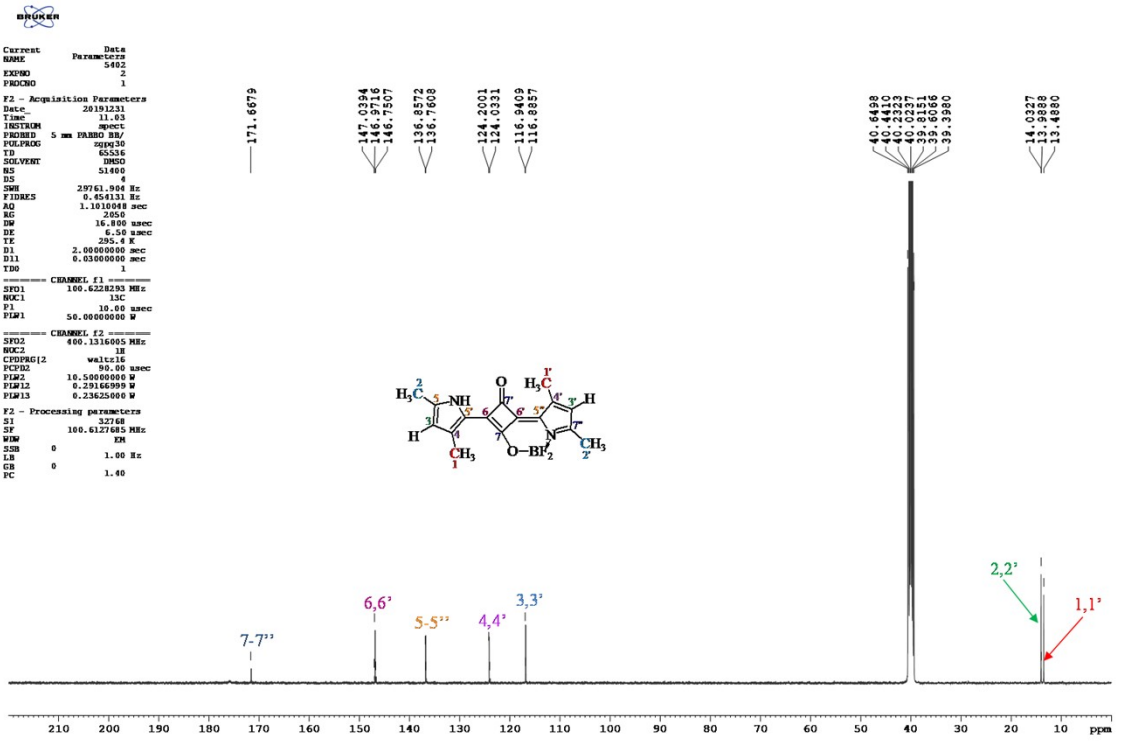


Figure S9 ^{13}C NMR spectra of 2,4-*bis*(3,5-dimethylpyrrol-2-yl)squaraine dichloroborate complex (BPSQ1) recorded in DMSO-d_6

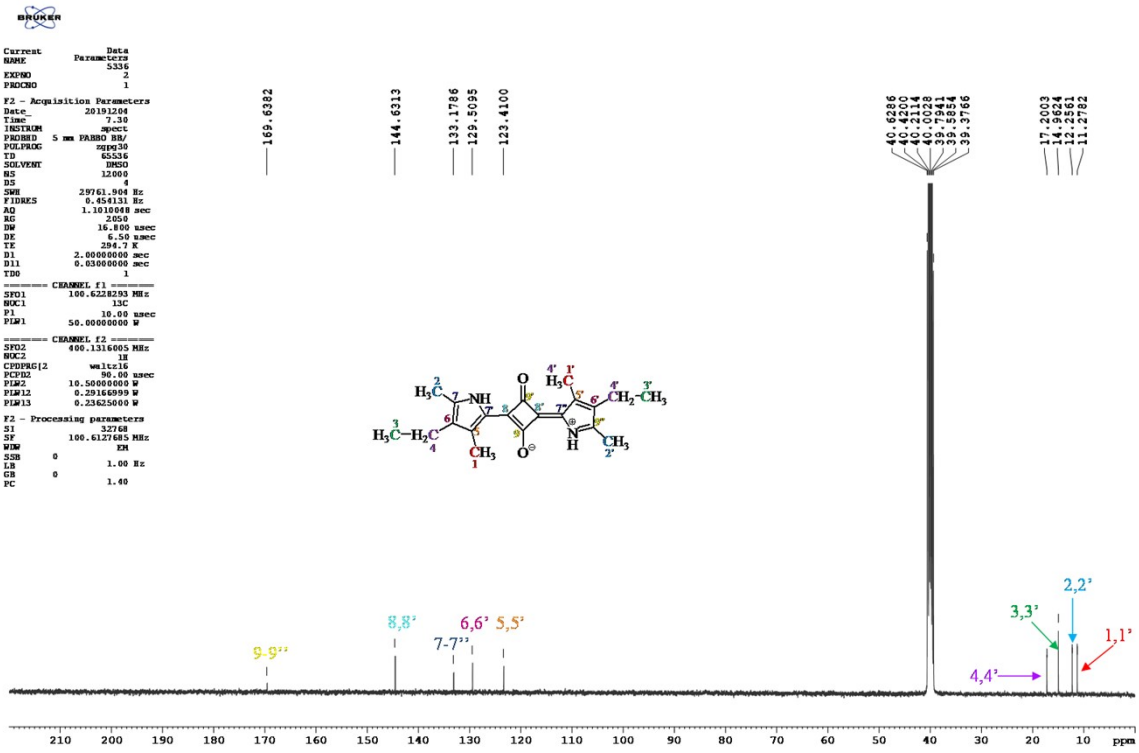


Figure S10 ^{13}C NMR spectra of 2,4-*bis*(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine (PSQ2) recorded in DMSO-d_6

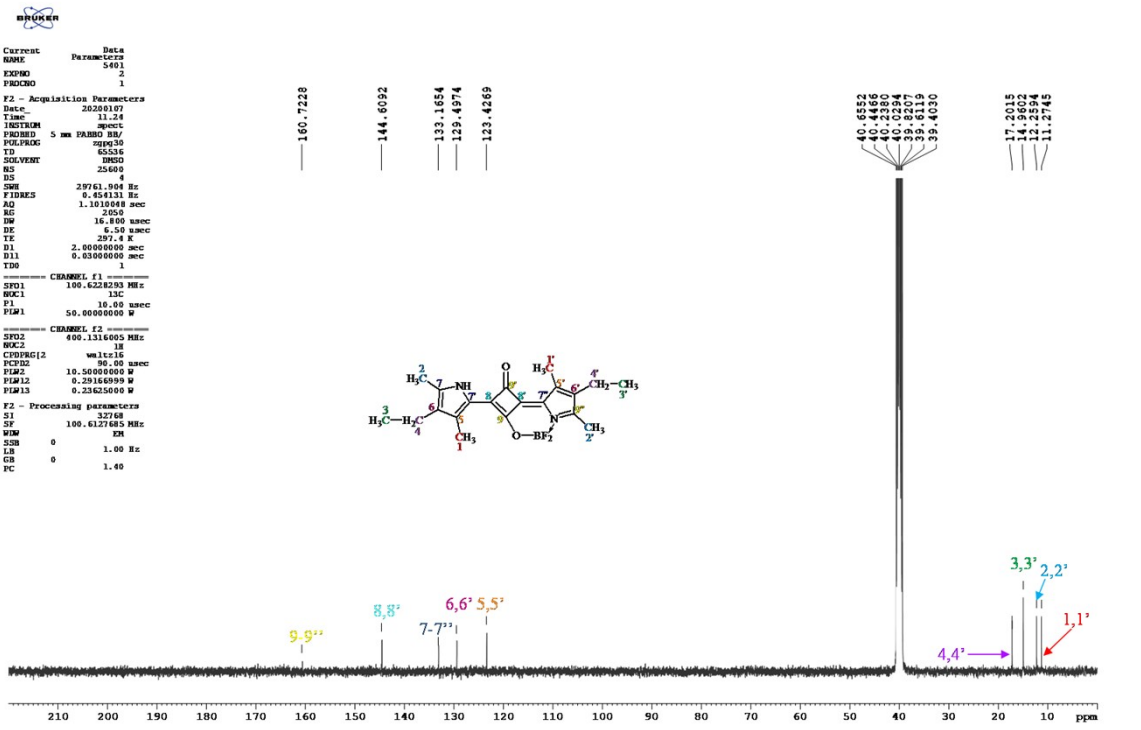


Figure S11 ^{13}C NMR spectra of 2,4-*bis*(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine dichloroborate complex (BPSQ2) recorded in DMSO-d_6

4. The procedure of synthesis of photosensitizers

2,4-*bis*(3,5-dimethylpyrrol-2-yl)squaraine (PSQ1)

A mixture of 0.63 g (5.2 mmol) of square acid and 1 g (~ 1.1 cm^3, 10.5 mmol) of 2,4-dimethylpyrrole in 50 cm^3 of anhydrous ethanol (99.8% anal) was heat under reflux for seven hours while stirring. The precipitated dye was filtered off and dried on air. Then it was crystallized from ethanol. Blue-violet dye crystals were obtained. The yield of the reaction was 75%.

2,4-*bis*(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine (PSQ2)

A mixture of 0.63 g (5.2 mmol) of square acid and 1.29 g (~ 1.42 cm^3, 10.5 mmol) of 3-ethyl-2,4-dimethylpyrrole in 50 cm^3 of anhydrous mixture of benzene/*n*-butanol (1:1) was heat under reflux for seven hours while stirring. The precipitated dye was filtered off and dried on air. Then it was crystallized from ethanol. Violet dye crystals were obtained. The yield of the reaction was 45%.

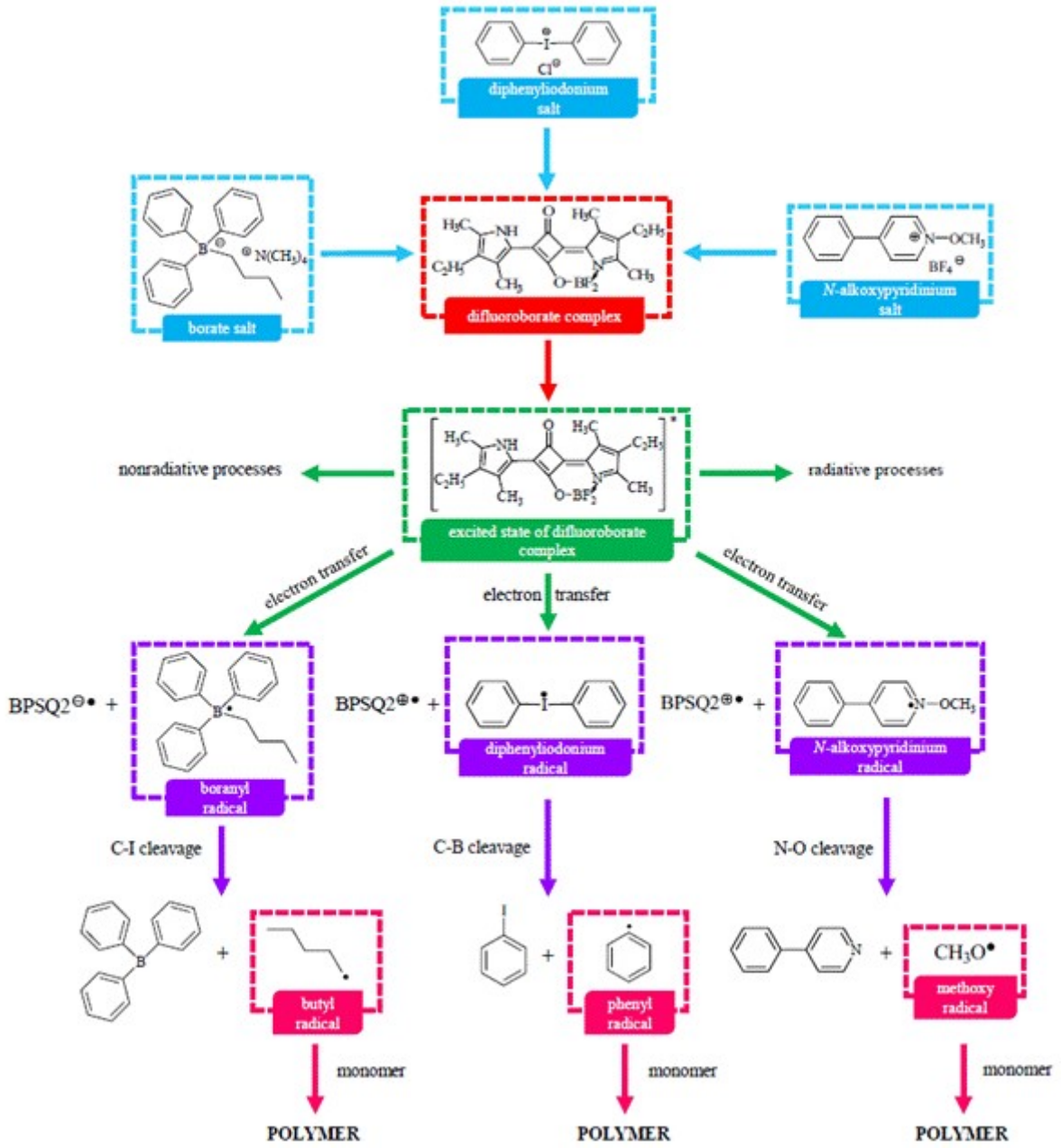
2,4-*bis*(3,5-dimethylpyrrol-2-yl)squaraine difluoroborate (BPSQ1)

200 mg (0.75 mmol) of the PSQ1 dye was dissolved in 100 cm^3 of anhydrous dichloromethane (99.8%). Then 1.04 cm^3 of anhydrous triethylamine (7.5 mmol) and 0.94 cm^3 (7.5 mmol) of anhydrous boron trifluoride diethyl etherate were added in a 10-fold molar excess and stirred at room temperature for two days. Then 200 cm^3 of water was added to the solution and it was extracted twice with 100 cm^3 of dichloromethane. The resulting blue-violet dye was filtered off and dried. The reaction yield was 43%.

2,4-*bis*(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine difluoroborate (BPSQ2)

100 mg (0,31 mmol) of the PSQ2 dye was dissolved in 40 cm^3 of anhydrous dichloromethane (99.8%). Then 0,43 cm^3 of anhydrous triethylamine (3.08 mmol) and 0.40 cm^3 (3.08 mmol) of anhydrous boron trifluoride diethyl etherate were added in a 10-fold molar excess and stirred at room temperature for two days. Then 150 cm^3 of saturated sodium chloride solution in water was added to the solution and it was extracted twice with 100 cm^3 of dichloromethane. The resulting blue-violet dye was filtered off and dried. The reaction yield was 53%.

5. The mechanism of free radical formation



Scheme S1. Mechanism of radical formation on the basis of photoinitiating systems composed of 2,4-*bis*(4-ethyl-3,5-dimethylpyrrol-2-yl)squaraine (PSQ2) and different co-initiators.