

## Supplementary information

# Highly sensitive photoinitiating system based on pre-associated ion-pairs for NIR radical photopolymerization of optically clear materials

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### Characterization of the borates

- Tetrabutylammonium tri(3-methyl-4-methoxyphenyl)-hexyl-borate (B1):

Synthesized following the general procedure using 3-methyl-4-methoxyphenylbromide as a starting material. The product was obtained as colorless crystals (52 g, 47%).

$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.21 (s, 3H), 7.19 – 7.15 (m, 3H), 6.57 (d,  $J$  = 8.0 Hz, 3H), 3.74 (s, 9H), 2.25 – 2.17 (m, 8H), 2.13 (s, 9H), 1.27 – 1.20 (m, 14H), 1.11 (m, 8H), 1.08 – 1.02 (m, 2H), 0.96 (t,  $J$  = 7.3 Hz, 12H), 0.85 (m, 5H).

$^{11}\text{B-NMR}$  (193 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -11.22.

- Tetrabutylammonium trianisylhexylborate (B2):

Synthesized following the general procedure using 4-methoxyphenylbromide as a starting material. The product was obtained as colorless crystals (57 g, 57%).

$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.33 (d,  $J$  = 7.8 Hz, 6H), 6.67 – 6.61 (m, 6H), 3.73 (s, 3H), 2.33 – 2.26 (m, 8H), 1.28 – 1.20 (m, 14H), 1.16 (m, 8H), 1.08 – 1.02 (m, 2H), 0.96 (t,  $J$  = 7.3 Hz, 12H), 0.92 – 0.88 (m, 2H), 0.82 (q,  $J$  = 5.1, 3.6 Hz, 3H).

$^{11}\text{B-NMR}$  (193 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = -11.1.

- Tetrabutylammonium tri(4-methylphenyl)-hexylborate (B4):

Synthesized following the general procedure using 4-methoxyphenylbromide as a starting material. The product was obtained as colorless crystals (58 g, 58%).

$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.29 (d,  $J$  = 7.2 Hz, 6H), 6.83 (d,  $J$  = 7.3 Hz, 6H), 2.21 (m, 17H), 1.21 (m, 14H), 1.09 (p,  $J$  = 7.9 Hz, 10H), 0.94 (t,  $J$  = 7.3 Hz, 12H), 0.91 – 0.87 (m, 2H), 0.85 – 0.81 (m, 3H).

$^{11}\text{B-NMR}$  (193 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = -10.8.

- Tetrabutylammonium tri(3-chloro-4-methylphenyl)-hexylborate (B6):

Synthesized following the general procedure using 3-chloro-4-methylphenylbromide as a starting material. The product was obtained as colorless crystals (48 g, 44%).

$^1\text{H-NMR}$  (400 MHz, DMSO)  $\delta$  (ppm) = 7.71 (s, 3H), 7.57 (d,  $J$  = 6.0 Hz, 3H), 7.31 (dd,  $J$  = 7.4, 0.8 Hz, 3H), 3.93 – 3.80 (m, 8H), 2.65 (s, 9H), 2.27 (m, 8H), 1.88 (h,  $J$  = 7.4 Hz, 8H), 1.74 – 1.64 (m, 6H), 1.55 – 1.46 (m, 2H), 1.43 (t,  $J$  = 7.4 Hz, 12H), 1.38 – 1.32 (m, 2H), 1.32 – 1.26 (m, 3H).

$^{11}\text{B-NMR}$  (193 MHz, DMSO)  $\delta$  (ppm) = -10.5.

- Tetrabutylammonium tri(3-chlorophenyl)-hexylborate (B7):

Synthesized following the general procedure using 3-chloro-phenylbromide as a starting material. The product was obtained as colorless crystals (56 g, 50%).

$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.28 (d,  $J = 7.4$  Hz, 3H), 7.00 (t,  $J = 7.5$  Hz, 3H), 6.85 (ddd,  $J = 7.8, 2.4, 1.2$  Hz, 3H), 2.45 (m, 3H), 1.24 (m, 22H), 0.96 (t,  $J = 6.9$  Hz, 14H), 0.91 – 0.85 (m, 2H), 0.85 – 0.82 (m, 3H).

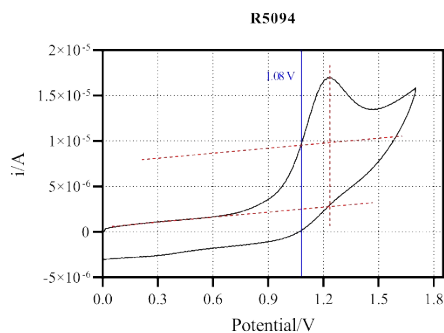
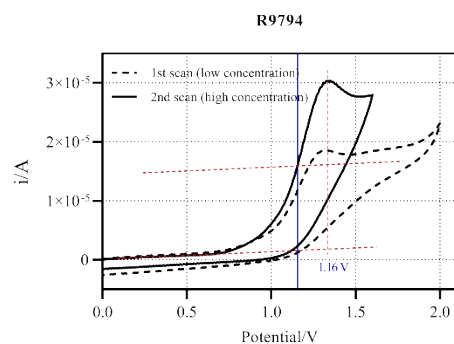
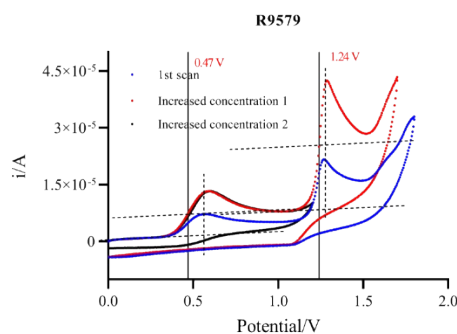
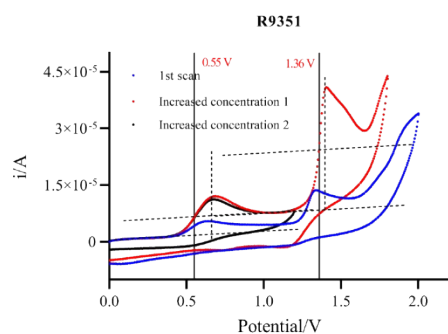
- Tetrabutylammonium tri(4-trifluoromethylphenyl)-hexylborate (B8):

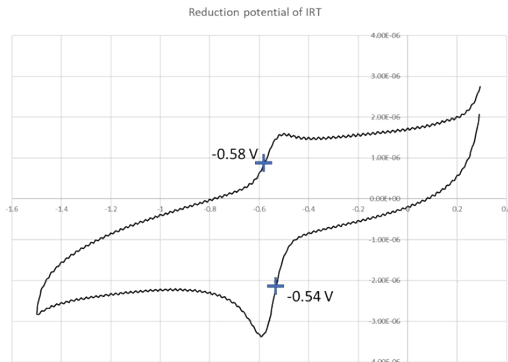
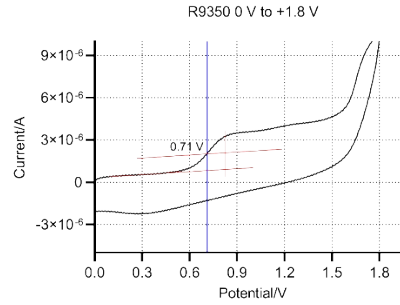
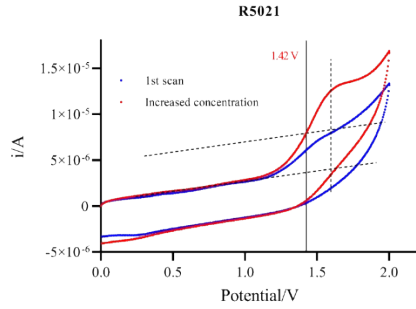
Synthesized following the general procedure using 4-trifluoromethylphenylbromide as a starting material. The product was obtained as colorless crystals (4.6 g, 22%).

$^1\text{H-NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) = 7.89 (d,  $J = 7.7$  Hz, 6H), 7.52 (d,  $J = 7.7$  Hz, 6H), 1.74-1.70 (m, 8H), 1.52-1.35 (m, 4H), 0.94 (t,  $J = 7.0$  Hz, 3H), 0.85-0.72 (m, 8H), 0.67 (t,  $J = 7.1$  Hz, 12H), 0.63-0.52 (m, 12H).

$^{11}\text{B-NMR}$ : (193 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) -9.8.

### Cyclic voltammetry





### Rate of polymerization in the framework of dynamic quenching

The rate of formation of excited states  $R_{exc}$  is calculated from:

$$R_{exc} = I_0 (1 - 10^{-\epsilon d [D]}) / d$$

with  $I_0$  the incident irradiance and  $d$  the photopolymer thickness of 20  $\mu\text{m}$ . Assuming an irradiance of 40  $\text{mW}/\text{cm}^2$  at 850 nm, a dye concentration of  $1.4 \cdot 10^{-3} \text{ M}$ , this leads to a rate of  $R_{exc} = 3.7 \cdot 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$ .

Knowing that the viscosity of the resin is 200  $\text{mPa}\cdot\text{s}$ , the quenching rate constant  $k_q$  can be estimated to be equal to the diffusion rate constant  $k_d$ . The later can be evaluated from the Stokes-Einstein equation:

$$k_q = k_d = \frac{8RT}{3\eta} = 3.3 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$$

The degree of quenching  $DE$  by the borate can be calculated from:

$$DE = 1 - \frac{1}{1 + k_q \tau_0 [\text{Borate}]}$$

From these values, the rate of initiation is:

$$R_{rad}^{init} = R_{exc} \cdot DE$$

Finally, from Figure 5b, the rate of polymerization is related to the rate of initiation through:

$$R_p = 16.93 (R_{rad}^{init})^{0.65}$$

Figure S11 shows the change in  $R_p$  with respect to the borate concentration. As can be seen, a quasi-linear relationship is found with rates of polymerization much lower than those determined.

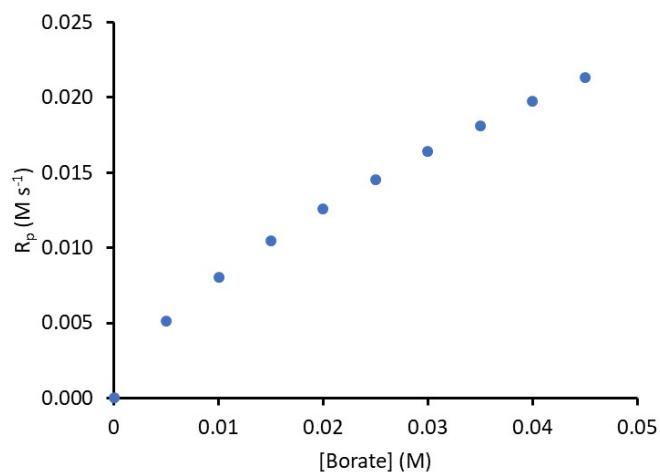


Figure S11. Calculated rate of polymerization assuming a dynamical quenching between the borate salt and IRT.

**Vibrationally-resolved computation of electronic spectra** were computed from Franck-Condon factors in the framework of harmonic model as obtained from the M062X/6-31G\* optimized structures of IRT ground state and first excited singlet state. The half-width at half-maximum of the vibrational lines is chosen at  $500\text{ cm}^{-1}$  for the convolution, assuming a Gaussian distribution. The final calculated vibronic spectra was obtained by applying the FC factors on the experimental vertical energy of the transition.

**Approximate dielectric constant  $\epsilon_s$**  of the mixture SR349/DMSO was calculated assuming:

$$\epsilon_s = \phi^{SR349} \epsilon_s^{SR349} + \phi^{DMSO} \epsilon_s^{DMSO}$$

$$\epsilon_s = 0.9 \times 7.03 + 0.1 \times 47.24 = 11.0$$

where  $\phi^{SR349}$  and  $\phi^{DMSO}$  are the volume ratio of SR349 and DMSO, respectively,  $\epsilon_s^{SR349}$  and  $\epsilon_s^{DMSO}$  being the corresponding dielectric constant. [Prakongpan, S., Nagai, T., 1984, Chem. Pharm. Bull. 32, 340–343.] the value  $\epsilon_s^{SR349}$  was taken equal to that of methylacrylate (7.03) and  $\epsilon_s^{DMSO}$  being 47.24. [Wohlfarth, *CRC Handbook of Chemistry and Physics*, 2004, **91**, 6-138]

#### **Absorption and fluorescence spectra in acetonitrile.**

Figure S12. Absorption spectrum of IRT in acetonitrile and corresponding fluorescence spectra recorded for excitation at 636 nm (Blue) and 751 nm (Red).

