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%).
  \[ ^1H-NMR \text{ (600 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) = 7.21 (s, 3H), 7.19 – 7.15 (m, 3H), 6.57 (d, } J = 8.0 \text{ Hz, 3H), 3.74 (s, 9H), 2.25 – 2.17 (m, 8H), 2.13 (s, 9H), 1.27 – 1.20 (m, 14H), 1.11 (m, 8H), 1.08 – 1.02 (m, 2H), 0.96 (t, } J = 7.3 \text{ Hz, 12H), 0.85 (m, 5H).} \]
  \[ ^{11}B-NMR \text{ (193 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) = -11.22.} \]

- **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%).
  \[ ^1H-NMR \text{ (600 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) = 7.33 (d, } J = 7.8 \text{ Hz, 6H), 6.67 – 6.61 (m, 6H), 3.73 (s, 3H), 2.33 – 2.26 (m, 8H), 1.28 – 1.20 (m, 14H), 1.16 (m, 8H), 1.08 – 1.02 (m, 2H), 0.96 (t, } J = 7.3 \text{ Hz, 12H), 0.92 – 0.88 (m, 2H), 0.82 (q, } J = 5.1, 3.6 \text{ Hz, 3H).} \]
  \[ ^{11}B-NMR \text{ (193 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) = -11.1.} \]

- **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%).
  \[ ^1H-NMR \text{ (600 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) = 7.29 (d, } J = 7.2 \text{ Hz, 6H), 6.83 (d, } J = 7.3 \text{ Hz, 6H), 2.21 (m, 17H), 1.21 (m, 14H), 1.09 (p, } J = 7.9 \text{ Hz, 10H), 0.94 (t, } J = 7.3 \text{ Hz, 12H), 0.91 – 0.87 (m, 2H), 0.85 – 0.81 (m, 3H).} \]
  \[ ^{11}B-NMR \text{ (193 MHz, CDCl}_3 \text{) } \delta \text{ (ppm) = -10.8.} \]

- **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%).
  \[ ^1H-NMR \text{ (400 MHz, DMSO) } \delta \text{ (ppm) = 7.71 (s, 3H), 7.57 (d, } J = 6.0 \text{ Hz, 3H), 7.31 (dd, } J = 7.4, 0.8 \text{ Hz, 3H), 3.93 – 3.80 (m, 8H), 2.65 (s, 9H), 2.27 (m, 8H), 1.88 (h, } J = 7.4 \text{ Hz, 8H), 1.74 – 1.64 (m, 6H), 1.55 – 1.46 (m, 2H), 1.43 (t, } J = 7.4 \text{ Hz, 12H), 1.38 – 1.32 (m, 2H), 1.32 – 1.26 (m, 3H).} \]
  \[ ^{11}B-NMR \text{ (193 MHz, DMSO) } \delta \text{ (ppm) = -10.5.} \]
- 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%).

\[ ^1H-NMR \ (600 \text{ MHz, } CDCl_3) \delta \ (ppm) = 7.28 \ (d, J = 7.4 \text{ Hz, } 3H), \ 7.00 \ (t, J = 7.5 \text{ Hz, } 3H), \ 6.85 \ (ddd, J = 7.8, 2.4, 1.2 \text{ Hz, } 3H), \ 2.45 \ (m, 3H), \ 1.24 \ (m, 22H), \ 0.96 \ (t, J = 6.9 \text{ Hz, } 14H), \ 0.91 – 0.85 \ (m, 2H), \ 0.85 – 0.82 \ (m, 3H). \]

- 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%).

\[ ^1H-NMR \ (600 \text{ MHz, } CDCl_3) \delta \ (ppm) = 7.89 \ (d, J = 7.7 \text{ Hz, } 6H), \ 7.52 \ (d, J = 7.7 \text{ Hz, } 6H), \ 1.74-1.70 \ (m, 8H), \ 1.52-1.35 \ (m, 4H), \ 0.94 \ (t, J = 7.0 \text{ Hz, } 3H), \ 0.85-0.72 \ (m, 8H), \ 0.67 \ (t, J = 7.1 \text{ Hz, } 12H), \ 0.63-0.52 \ (m, 12H). \]

\[ ^11B-NMR: \ (193 \text{ MHz, } CDCl_3) \delta \ (ppm) -9.8. \]

Cyclic voltammetry

![Cyclic voltammetry graphs](image-url)
Rate of polymerization in the framework of dynamic quenching

The rate of formation of excited states \( R_{\text{exc}} \) is calculated from:

\[
R_{\text{exc}} = I_0 \left( 1 - 10^{-c_d[D]} \right)/d
\]

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

Knowing that the viscosity of the resin is 200 mPa.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:

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

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:

\[
R_{\text{init}}^{\text{rad}} = R_{\text{exc}} \cdot DE
\]

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

\[
R_p = 16.93 \left( R_{\text{rad,init}} \right)^{0.65}
\]
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.

![Graph showing change in $R_p$ with respect to borate concentration.](image)

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 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** $\varepsilon_S$ of the mixture SR349/DMSO was calculated assuming:

$$\varepsilon_S = \phi_{SR349}\varepsilon_{SR349} + \phi_{DMSO}\varepsilon_{DMSO}$$

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

where $\phi_{SR349}$ and $\phi_{DMSO}$ are the volume ratio of SR349 and DMSO, respectively, $\varepsilon_{SR349}$ and $\varepsilon_{DMSO}$ being the corresponding dielectric constant. [Prakongpan, S., Nagai, T., 1984, Chem. Pharm. Bull. 32, 340–343.] the value $\varepsilon_{SR349}$ was taken equal to that of methylacrylate (7.03) and $\varepsilon_{DMSO}$ 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).