

Supporting Information

**New Iodonium Salts in NIR Sensitized Radical Photopolymerization of
Multifunctional Monomers**

Thomas Brömme, Dennis Oprych, Joachim Horst, Paula Sevenini Pinto,

*Bernd Strehmel**

^{a)}Department of Chemistry and ^{b)}Institute for Coatings and Surface Chemistry, Niederrhein
University of Applied Sciences, Adlerstr. 32, D-47798 Krefeld, Germany

Material Synthesis

Symmetric iodonium salts

438 ml conc. H₂SO₄ were placed to a four-neck round bottom flask to which 0.5 mol I₂ and 0.75 mol KIO₃ were continuously added under continuous stirring at 10°C. The brown suspension obtained turns later into a yellow suspension within 1 h. Small amounts of KIO₃ (2-3 g) were added if brown smears remained in the suspension, followed by additional stirring for 30 min. The suspension obtained was cooled to 0-10°C followed by adding of 3 mol (CH₃CO)₂O into the suspension. The temperature should not increase >15°C while after completion stirring was continued for additional 30 min. This solution was transferred into a second four-neck flask containing 2.5 mol aromat, where the reaction mixture was continuously stirred. Temperature should locate between 3-15°C at this reaction step. After completion, the reaction mixture was stirred for additional 2-3 h. Subsequently, the suspension was poured into a beaker containing 400 g ice resulting in separation into an organic and aqueous phase. Both phases were separated, whereupon the aqueous phase was mixed with 250 ml saturated KBr or NH₄Cl solution (aq.) resulting in formation of a slight yellow precipitate. This was filtered and washed three times with MEK. Furthermore, the brown organic phase was mixed with 500 ml saturated KBr or NH₄Cl solution (aq.) under

stirring. The slowly crystallized product was washed with MEK and dried in a vacuum at room temperature for one day, followed by an additional drying procedure at 55°C. Both crystalline materials were merged together resulting in a yield between 5-71% depending on substitution of the aromat (bis(4-*t*-butylphenyl)iodonium chloride: 66%, mp: 213°C; bis(4-*t*-butylphenyl)iodonium bromide: 71%, mp: 176°C; bis(4-isopropylphenyl)iodonium chloride: 66%, mp: 169-172°C; bis(2,4-diisopropylphenyl)iodonium chloride: 17%, mp: 143-148°C; bis(2,4,6-trimethylphenyl)iodonium chloride: 8%, mp: 127-133°C; bis(methylphenyl)iodonium bromide: 43%, mp: 203-213°C)

Asymmetric iodonium salts

(*i*-Pentoxy)benzene was synthesized according the ether synthesis by Williamson (Chemistry Schwetlick, K., Organikum, 2015, ISBN 978-3-527-33968-6). Thus, 1 mol sodium phenolate dehydrate and 1.25 mol (3-methyl-butyl)bromide were placed in a four neck flask. 250 ml DMSO were dropped to this mixture under continuous stirring followed by adding of 0.2 mmol KI. After 5 h refluxing, this mixture was poured into 2 L of distilled water. The isolated organic phase was dried over Na₂SO₄ and finally distilled (1013 mbar, 230 °C) (yield: 43 %; mp: °C). The (*i*-pentoxy)benzene was used for further synthesis of the asymmetric iodonium salt. Thus, 367 mmol CrO₃, 250 mL CH₃COOH, and 120 mL (CH₃CO)₂O were placed in a four-neck flask followed by addition of 500 mmol Iodobenzen and 85 mL conc. H₂SO₄ at room temperature. This occurred under continuous stirring. After 30 min, 550 mmol (*i*-pentoxy)benzene was added at room temperature. The solution obtained was stirred for an additional hour following by transferring into 1.3 L of an aqueous methanol solution (30 wt-%). Finally, 350 mL of a saturated KBr solution were added, stirred for additional 5 h while a slight yellow precipitate was formed. This was isolated by filtration, washed twice with cold water and finally with acetone. The collected 4-Isopentoxyphenylphenyliodonium bromide was finally dried in vacuum at 40°C (yield: 58 %; mp: 163-167°C).

Anion changing Method A: The iodonium halide and sodium tetraphenylborate were separately dissolved in *i*-PrOH at room temperature. Both solutions were put together resulting in a white precipitate, which was finally stirred for 1 h, filtered, and washed with *i*-PrOH. The wet iodonium tetraphenylborate was dried in a vacuum drying cabinet at room temperature for one day, followed by an additional drying at 55°C.

Anion changing Method B: The inorganic salt comprising the anion (available as sodium or lithium salt) and the iodonium halide were mixed (1:1), dissolved in a chloroform/deionized water (1:1) solution, and stirred for 1 h. The organic phase was

separated, washed three times with deionized water, and filtered over anhydrous sodium sulfate. The solvent was evaporated in vacuum. The residue obtained was dried at room temperature in a vacuum for one day, followed by an additional drying procedure at 65°C.

Anion changing Method C: The water sensitive anion tetrakis(pentafluorophenyl)borate, available as lithium salt, and the iodonium halide were mixed (1:1), dissolved in a chloroform/diethylether (1:1) solution, and stirred for 1 h. The precipitate was removed while the solution was concentrated and dried at room temperature in a vacuum for one day, followed by an additional drying at 40°C.

Anion changing Method D: Benzilic acid and the iodonium halide were (1:1) dissolved in chloroform, and stirred for 1 h. The organic phase obtained was washed once with aqueous saturated sodium hydrogencarbonate solution, followed with three times washing with deionized water, and final filtration over sodium sulfate. The filtrate was pre-dried at room temperature in a vacuum for one day, followed by an additional drying procedure at 40°C.

Anion changing Method E: For this anion changing method uses a silver salt comprising the anion needed for exchange. AgNO_3 and an inorganic salt comprising anion needed for exchange were separately dissolved in deionized water at room temperature. Both solutions were unified resulting in a white precipitate, which was finally stirred for 10 min. The precipitate was isolated and twice washed with a small amount of cold deionized water. The precipitate obtained was dried at room temperature in a vacuum for one day, followed by an additional drying procedure at 60°C. The iodonium halide and the silver salt comprising the anion needed for exchange were dissolved equimolar in methanol, and stirred for 1 h. The precipitate was washed three times with methanol while the filtrates were collected and the solvent was evaporated in vacuum. The obtained iodonium salt was finally dried at room temperature in a vacuum for one day followed by an additional drying at 40°C.

Anion changing Method F: The iodonium halide and silver nitrate were dissolved equimolar in warm deionized water, and stirred for 1 h. The precipitate was isolated and additionally washed three times with warm deionized water. The filtrates were unified followed by water removal in vacuum. The iodonium nitrate was finally dried at 65°C in a vacuum.

Bis(4-*t*-butylphenyl)iodonium tetraphenylborate (1a). This compound was made according to method A. It was isolated in 99% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.65 – 7.54 (m, 8H), 7.33 (s, 8H), 7.02 (t, $J = 7.4$ Hz, 8H), 6.82 (t, $J = 7.2$ Hz, 4H), 1.28 (s, 18H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 165.72, 165.07, 164.42, 163.77, 156.77, 136.32, 136.29, 134.22, 129.55, 126.58, 126.55, 126.51, 126.48, 122.52, 110.04, 109.96, 77.51, 77.09, 76.67, 64.48, 35.28, 31.00, 25.40; IR (FTIR): 2960, 1477, 1392, 1106, 989, 821, 704, 605, 541; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.22, anion $\text{C}_{24}\text{H}_{20}\text{B}^-$: 319.23, found 319.02; mp: 158-166 °C.

Bis(4-*t*-butylphenyl)iodonium tetrakis(pentafluorophenyl)borate (1b). This compound was made according to method C. It was isolated in 80% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.79 – 7.72 (m, 4H), 7.56 – 7.49 (m, 4H), 1.30 (s, 18H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 158.71, 149.82, 146.64, 139.84, 137.95, 136.57, 134.52, 130.87, 108.37, 77.49, 77.27, 77.07, 76.64, 65.88, 35.47, 30.75, 15.28; IR (FTIR): 2971, 1511, 1464, 1277, 1093, 979, 818; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.26, anion $\text{C}_{24}\text{F}_{20}\text{B}^-$: 679.04, found 679.11; mp: 77-79 °C.

Bis(4-*t*-butylphenyl)iodonium tetracyanoborate (1c). This compound was made according to method B. It was isolated in 81.9% yield as slightly yellow powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.92 – 7.81 (m, 4H), 7.59 – 7.47 (m, 4H), 1.31 (s, 18H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 157.14, 134.66, 130.19, 124.09, 123.15, 122.20, 121.25, 110.93, 77.62, 77.40, 77.20, 76.77, 46.33, 40.20, 35.39, 31.01, 21.81; IR (FTIR): 2966, 1480, 1395, 1106, 990, 925, 824, 541; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.20; mp: 93-107 °C.

Bis(4-*t*-butylphenyl)iodonium benzilate (1d). This compound was made according to method D. It was isolated in 85% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.65 – 7.54 (m, 4H), 7.54 – 7.43 (m, 6H), 7.37 – 7.13 (m, 8H), 5.81 – 5.78 (m, 1H), 1.29 (s, 18H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 154.34, 134.45, 128.48, 116.11, 77.60, 77.17, 76.75, 34.95, 31.10, 31.08; IR (FTIR): 2961, 1671, 1167, 697, 542; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.29, calculated anion $\text{C}_{14}\text{H}_{11}\text{O}_3^-$: 227.24, found 226.88; mp: 132-145 °C.

Bis(4-*t*-butylphenyl)iodonium lactate (1e). This compound was made according to method E. It was isolated in 91.8% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.92

– 7.80 (m, 4H), 7.43 – 7.32 (m, 4H), 4.14 (s, 1H), 3.69 (q, $J = 6.8$ Hz, 1H), 1.28 (s, 18H), 1.01 (d, $J = 6.8$ Hz, 3H); ^{13}C -NMR (75 MHz, CDCl_3) δ 180.29, 134.35, 128.50, 114.81, 77.69, 77.27, 76.84, 67.68, 40.24, 34.99, 31.04, 21.84, 20.85; IR (FTIR): 3423, 2963, 1562, 1341, 1109, 819, 547; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.30, mp: 145-155 °C.

Bis(4-*t*-butylphenyl)iodonium nitrate (1f). This compound was made according to method F. This compound was isolated in 99% yield as white powder: ^1H -NMR (300 MHz, Chloroform-*d*) δ 7.93 (d, $J = 8.4$ Hz, 4H), 7.38 (d, $J = 8.4$ Hz, 4H), 1.27 (s, 18H); ^{13}C -NMR (75 MHz, CDCl_3) δ 154.77, 134.70, 128.72, 115.04, 77.74, 77.31, 76.89, 46.40, 40.28, 35.03, 31.09, 21.89; IR (FTIR): 2961, 1287, 1106, 994, 821, 541; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.28; mp: 176 °C.

Bis(4-*t*-butylphenyl)iodonium perfluorobutanesulfonate (1j). This compound was made according to method B. It was isolated in 92.2% yield as bright brown powder: ^1H -NMR (300 MHz, Chloroform-*d*) δ 7.95 – 7.84 (m, 4H), 7.50 – 7.38 (m, 4H), 1.29 (s, 18H); ^{13}C -NMR (75 MHz, CDCl_3) δ 156.15, 135.07, 129.31, 110.60, 77.55, 77.13, 76.70, 46.24, 40.12, 35.14, 30.92, 21.73; IR (FTIR): 2967, 1235, 1133, 1054, 654, 542; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.32, calculated anion $\text{C}_4\text{F}_9\text{O}_3\text{S}^-$: 299.09, found 298.90; mp: 173-176 °C.

Bis(4-*t*-butylphenyl)iodonium dodecylbenzensulfonate (1k). This compound was made according to method B. It was isolated in 89.5% yield as yellow powder: ^1H -NMR (300 MHz, Chloroform-*d*) δ 7.92 – 7.76 (m, 4H), 7.58 (dd, $J = 8.2, 2.0$ Hz, 2H), 7.45 – 7.33 (m, 4H), 7.04 (dd, $J = 10.8, 8.2$ Hz, 2H), 1.73 – 1.37 (m, 4H), 1.29 (s, 18H), 1.27 – 0.95 (m, 15H), 0.93 – 0.65 (m, 6H); ^{13}C -NMR (75 MHz, CDCl_3) δ 155.00, 149.26, 147.81, 147.75, 147.49, 143.08, 143.03, 134.93, 128.77, 127.18, 127.11, 126.45, 126.09, 126.03, 112.94, 47.69, 45.85, 45.56, 39.76, 39.16, 38.37, 36.98, 36.93, 36.67, 36.56, 35.05, 32.00, 31.93, 31.89, 31.80, 31.08, 29.81, 29.77, 29.71, 29.66, 29.63, 29.56, 29.44, 29.37, 29.34, 29.27, 27.69, 27.61, 27.55, 27.26, 22.78, 22.70, 22.67, 22.59, 22.33, 20.61, 14.16, 14.12, 14.06, 12.19; IR (FTIR): 2958, 2924, 2855, 1481, 1171, 1007, 542; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.30, anion $\text{C}_{18}\text{H}_{29}\text{O}_3\text{S}^-$: 325.49, found 325.34; mp: 82-92 °C.

Bis(4-*t*-butylphenyl)iodonium styrenesulfonate (1l). This compound was made according to method B. It was isolated in 83.3% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.92 – 7.80 (m, 4H), 7.64 – 7.54 (m, 2H), 7.40 – 7.21 (m, 6H), 6.66 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.72 (dd, $J = 17.6, 0.9$ Hz, 1H), 5.25 (dd, $J = 10.8, 0.9$ Hz, 1H), 1.27 (s, 18H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 155.50, 144.91, 138.46, 136.33, 134.86, 128.99, 126.36, 125.71, 114.69, 111.46, 77.48, 77.05, 76.63, 35.09, 31.04; IR (FTIR): 2960, 1168, 1003, 673, 545; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.20, calculated anion $\text{C}_8\text{H}_7\text{O}_3\text{S}^-$: 183.20, found 182.80; mp: 180-189 °C.

Bis(4-*t*-butylphenyl)iodonium dicyanoimide (1m). This compound was made according to method E. It was isolated in 99% yield as beige powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 4H), 7.52 – 7.41 (m, 4H), 1.29 (d, $J = 1.6$ Hz, 18H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 155.97, 134.61, 129.44, 119.96, 112.01, 35.22, 31.06; IR (FTIR) 2960, 2229, 2124, 1479, 1392, 1106, 993, 817, 540; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.34; mp: 91-95 °C.

Bis(4-*t*-butylphenyl)iodonium bis(trifluoromethylsulfonyl)imide (1n). This compound was made according to method B. It was isolated in 87.9% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 8.00 – 7.87 (m, 4H), 7.57 – 7.44 (m, 4H), 1.30 (s, 18H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 157.47, 135.10, 130.18, 126.14, 121.88, 117.62, 113.36, 108.33, 77.55, 77.13, 76.70, 44.05, 35.33, 31.07, 30.90, 30.69, 17.76; IR (FTIR): 2967, 1351, 1299, 1184, 1127, 508; MS (ESI) calculated for cation $\text{C}_{20}\text{H}_{26}\text{I}^+$: 393.32, found 393.21, calculated anion $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$: 280.15, found 297.81; mp: 153-154 °C.

Bis(4-*i*-propylphenyl)iodonium tetrakis(pentafluorophenyl)borate (2b). This compound was made according to method C. It was isolated in 76% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.76 – 7.67 (m, 4H), 7.36 – 7.27 (m, 4H), 2.92 (hept, $J = 6.9$ Hz, 2H), 1.20 (d, $J = 6.9$ Hz, 12H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 155.45, 149.81, 146.63, 139.80, 137.89, 136.56, 134.62, 131.30, 110.58, 77.49, 77.28, 77.07, 76.65, 34.13, 23.37; IR (FTIR): 2971, 1511, 1464, 1277, 1093, 979, 818; MS (ESI) calculated for cation $\text{C}_{18}\text{H}_{22}\text{I}^+$: 365.27, found 365.20, calculated anion $\text{C}_{24}\text{F}_{20}\text{B}^-$: 679.04, found 679.05; mp: 52-57 °C.

Bis(4-*i*-propylphenyl)iodonium bis(trifluoromethylsulfonyl)imide (2n). This compound was made according to method B. It was isolated in 81.3% yield as orange/yellow adhesive

powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.98 – 7.86 (m, 4H), 7.40 – 7.29 (m, 4H), 2.94 (hept, $J = 6.9$ Hz, 2H), 1.22 (d, $J = 6.9$ Hz, 12H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 155.05, 135.37, 131.10, 126.17, 121.91, 117.65, 113.39, 108.92, 77.53, 77.10, 76.68, 34.12, 23.50; IR (FTIR): 2966, 1347, 1180, 1127, 1052, 598, 569, 508; MS (ESI) calculated for cation $\text{C}_{18}\text{H}_{22}\text{I}^+$: 365.27, found 365.19, calculated anion $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$: 280.15, found 279.90; mp: 47-49 °C.

Bis(*p*-methylphenyl)iodonium nitrate (3f). This compound was made according to method F. It was isolated in 81.3% yield as white powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 8.11 (dd, $J = 8.0, 1.3$ Hz, 0H), 7.90 – 7.81 (m, 4H), 7.80 – 7.72 (m, 1H), 7.40 (dd, $J = 7.6, 1.8$ Hz, 0H), 7.19 (d, $J = 8.0$ Hz, 4H), 2.59 (s, 1H), 2.35 (d, $J = 3.4$ Hz, 6H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 142.76, 141.20, 137.42, 134.86, 134.28, 132.86, 132.66, 131.69, 129.35, 120.27, 111.66, 110.83, 77.51, 77.28, 77.09, 76.66, 25.67, 21.42, 21.36; IR (FTIR): 1300, 804, 476; MS (ESI) calculated for cation $\text{C}_{14}\text{H}_{14}\text{I}^+$: 309.16, found 309.31; mp: 125-130 °C.

Bis(*p*-methylphenyl)iodonium bis(trifluoromethylsulfonyl)imide (3n). This compound was made according to method B. It was isolated in 78% yield as darkbrown powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 8.05 (d, 0H), 7.91 – 7.73 (m, 4H), 7.61 – 7.41 (m, 1H), 7.31 – 7.21 (m, 4H), 2.59 (s, 1H), 2.37 (s, 6H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 144.25, 144.19, 141.21, 137.17, 135.11, 134.86, 133.82, 133.53, 133.43, 132.39, 130.17, 126.19, 121.93, 118.91, 117.67, 113.41, 109.99, 108.72, 77.54, 77.11, 76.69, 25.56, 21.37; IR (FTIR): 1342, 1175, 1051, 797, 598, 568, 508, 472; MS (ESI) calculated for cation $\text{C}_{14}\text{H}_{14}\text{I}^+$: 309.16, found 309.12, calculated anion $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$: 280.15, found 279.90.

Bis(2,4,6-trimethylphenyl)iodonium bis(trifluoromethylsulfonyl)imide (5n). This compound was made according to method B. It was isolated in 90.4% yield as bright brown powder: $^1\text{H-NMR}$ (300 MHz, Chloroform-*d*) δ 7.09 (s, 2H), 2.49 (s, 6H), 2.34 (s, 3H); $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) δ 144.48, 142.19, 131.32, 126.21, 121.95, 117.69, 116.49, 113.43, 77.55, 77.13, 76.70, 41.30, 35.17, 25.98, 20.86, 16.78; IR (FTIR): 1337, 1181, 1052, 608, 511; MS (ESI) calculated for cation $\text{C}_{14}\text{H}_{14}\text{I}^+$: 365.27, found 365.12, calculated anion $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$: 280.15, found 279.90; mp: 90-92 °C.

Bis(2,4-diisopropylphenyl)iodonium bis(trifluoromethylsulfonyl)imide (6n). This compound was made according to method B. It was isolated in 92.4% yield as beige oil: $^1\text{H-NMR}$

NMR (300 MHz, Chloroform-*d*) δ 7.72 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 2.3$ Hz, 2H), 7.17 (dd, $J = 8.5, 2.3$ Hz, 2H), 3.00 (dp, $J = 24.9, 6.8$ Hz, 4H), 1.25 (dd, $J = 6.9, 1.0$ Hz, 24H); ^{13}C -NMR (75 MHz, CDCl_3) δ 155.92, 150.68, 136.35, 129.16, 127.49, 126.21, 121.95, 117.69, 113.43, 112.86, 77.51, 77.09, 76.67, 38.39, 34.21, 23.83, 23.62; IR (FTIR): 2966, 1345, 1178, 1132, 1052, 613, 569, 510; MS (ESI) calculated for cation $\text{C}_{24}\text{H}_{34}\text{I}^+$: 449.43, found 449.19, calculated anion $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$: 280.15, found 279.90.

[4-(*i*-Pentoxy)phenyl]phenyliodonium tetraphenylborate (7a). This compound was made according to method B. It was isolated in 94.4% yield as yellow powder: ^1H -NMR (300 MHz, Chloroform-*d*) δ 7.62 – 7.52 (m, 8H), 7.49 – 7.27 (m, 2H), 7.21 – 6.91 (m, 13H), 6.76 (t, $J = 7.3$ Hz, 4H), 6.62 (dd, $J = 8.6, 2.7$ Hz, 2H), 3.89 – 3.78 (m, 2H), 1.77 (dh, $J = 13.6, 6.9, 6.5$ Hz, 1H), 1.61 (q, $J = 6.8$ Hz, 2H), 0.92 (dd, $J = 7.0, 2.6$ Hz, 6H); ^{13}C -NMR (75 MHz, CDCl_3) δ 165.71, 165.38, 165.06, 164.40, 163.75, 162.59, 137.56, 136.79, 136.38, 134.85, 133.92, 132.49, 132.35, 132.24, 131.21, 130.41, 128.90, 128.47, 128.06, 127.26, 126.65, 126.59, 122.65, 118.50, 114.70, 101.62, 77.65, 77.43, 77.23, 76.80, 67.23, 37.64, 25.02, 22.65; IR (FTIR): 3052, 2956, 1578, 1469, 1253, 731, 702, 605; MS (ESI) calculated for cation $\text{C}_{17}\text{H}_{20}\text{IO}^+$: 367.24, found 367.33, calculated anion $\text{C}_{24}\text{H}_{20}\text{B}^-$: 319.23, found 319.12; mp: 55-59°C.

[4-(*i*-Pentoxy)phenyl]phenyliodonium bis(trifluoromethylsulfonyl)imide (7n). This compound was made according to method B. It was isolated in 93% yield as beige powder: ^1H -NMR (300 MHz, Chloroform-*d*) δ 7.97 – 7.84 (m, 4H), 7.63 – 7.48 (m, 1H), 7.42 (dd, $J = 8.5, 7.2$ Hz, 2H), 7.00 – 6.87 (m, 2H), 3.96 (t, $J = 6.6$ Hz, 2H), 1.78 (dp, $J = 13.2, 6.6$ Hz, 1H), 1.64 (q, $J = 6.6$ Hz, 2H), 0.93 (d, $J = 6.6$ Hz, 6H); ^{13}C -NMR (75 MHz, CDCl_3) δ 162.75, 137.60, 134.57, 132.46, 132.35, 126.20, 121.93, 118.72, 117.67, 115.45, 113.42, 102.26, 77.52, 77.30, 77.10, 76.67, 67.17, 37.54, 24.92, 22.46; IR (FTIR): 2958; 1568; 1470; 1351; 1253; 1173; 1052; 735; 612; MS (ESI) calculated for cation $\text{C}_{17}\text{H}_{20}\text{IO}^+$: 367.24, found 367.28, calculated anion $\text{C}_2\text{F}_6\text{NO}_4\text{S}_2^-$: 280.15, found 279.81; mp: 116-117°C.

Reactivity and solubility data

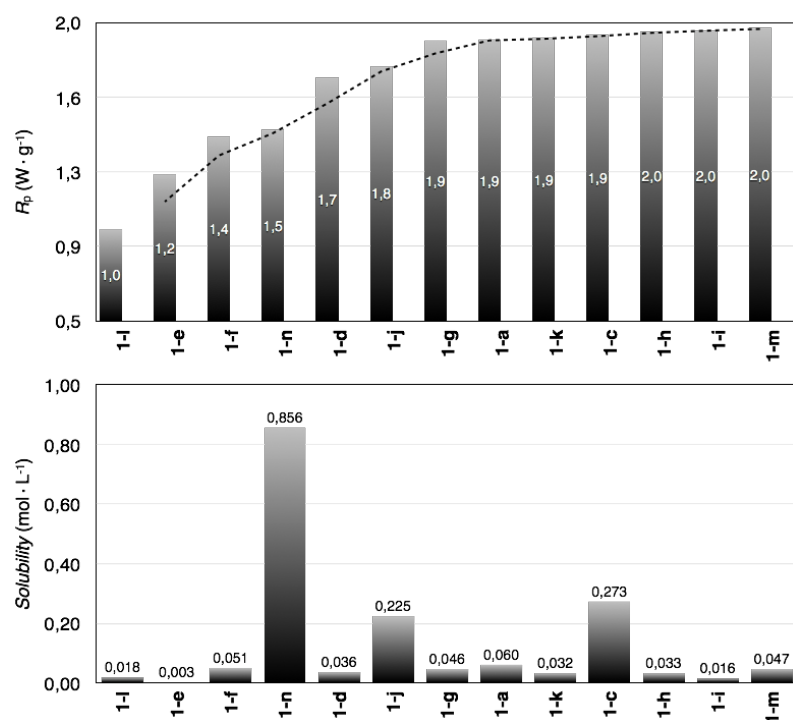


Figure S1. Comparison of reactivity (maximum of polymerization rate R_p determined by photo-DSC with a NIR-LED array emitting at 778 nm) and molar solubility of iodonium salts comprising cation **1** and different anions in the monomer **M3**, **S1**: 0.06 wt-%, **1n**: 1 wt-%, exposure was carried out with a NIR-LED array emitting at 780 nm using a photo-DSC for reactivity evaluation.

Table S1: Summary of solubility data of different iodonium salts exhibiting outstanding solubility (**1n-6n**) and their comparison with other salts (**1b, 2b, 4b, 8g, 8h**).

cation	anion	molecular weight in g·mol ⁻¹	Solubility (M1) in g·L ⁻¹ (in mol·L ⁻¹)	Solubility (M2) in g·L ⁻¹ (in mol·L ⁻¹)	Solubility (M4) in g·L ⁻¹ (in mol·L ⁻¹)	Solubility (M3) in g·L ⁻¹ (in mol·L ⁻¹)
1	n	673.47	501 (0.74)	343 (0.50)	449 (0.66)	576 (0.85)
2	n	644.99	>2000 (>3.1)	>2000 (>3.1)	>2000 (>3.1)	>2000 (>3.1)
3	n	588.93	>2000 (>3.4)	>2000 (>3.4)	>2000 (>3.4)	>2000 (>3.4)
5	n	644.99	302 (0.46)	174 (0.27)	306 (0.47)	191 (0.29)
6	n	729.58	>2000 (>2.7)	>2000 (>2.7)	>2000 (>2.7)	>2000 (>2.7)
7	n	647.39	409 (0.63)	325 (0.50)	254 (0.39)	235 (0.36)
1	b	1072.36	482 (0.45)	289 (0.27)	268 (0.25)	209 (0.19)
2	b	1044,31	308 (0.29)	183 (0.17)	146 (0.14)	100 (0.09)
4	b	1030.28	58 (0.057)	58 (0.058)	47 (0.046)	16 (0.016)
8	g	554.29	39 (0.070)	86 (0.156)	51 (0.092)	51 (0.092)
8	h	645.07	241 (0.37)	240 (0.37)	144 (0.22)	211 (0.32)