Supporting Information

TiO$_2$ nanocomposites with high refractive index and transparency

Peng Tao,$^a$ Yu Li,$^b$ Atri Rungta,$^b$ Anand Viswanath,$^b$ Jianing Gao,$^a$
Brian C. Benicewicz,$^b$ Richard W. Siegel,$^a$ Linda S. Schadler$^{a,*}$

$^a$Department of Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York 12180,

$^b$Department of Chemistry and Biochemistry and USC Nanocener, University of South Carolina, Columbia, South Carolina 29208

*to whom correspondence should be addressed: schadl@rpi.edu
Synthesis of phosphate-azide ligand

(1) Synthesis of 2-hydroxyethyl 2-bromo-2-methylpropanoate

To a 250 mL round-bottom dry flask was added anhydrous ethylene glycol (55 mL, 1 mol). The flask was put into an ice bath and stirred with magnetic stir bar. And then 2-bromoisobutyl bromide (5 mL, 40 mmol) was added dropwise into the flask. The solution was stirred for 3 hours and quenched with 25 mL DI water. The solution was extracted with CH$_2$Cl$_2$ (3 × 25 mL), dried with sodium sulfate overnight, and filtered. After the removal of the solvent by a rotoevaporator, 2-bromo-2methyl-propionic acid 2-hydroxyl ester was obtained as a colorless liquid (yield: 8.2 g, 82.5%). $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 4.4 (t, 2H), 3.85 (t, 2H), 3.26 (s, 1H), 1.89 (s, 6H)

(2) Synthesis of 2-hydroxyethyl 2-azido-2-methylpropanoate

To a 250 mL round-bottom dry flask was added anhydrous DMF (60 mL), 2-bromo-2methyl-propionic acid 2-hydroxyl ester (8.2 g, 38.8 mmol) and NaN$_3$ (2.7 g, 41.55 mmol). The solution was stirred with magnetic bar for 24 hours at ambient temperature and quenched with DI water (80 mL). The solution was extracted with CH$_2$Cl$_2$ (3 × 50 mL), re-extracted with DI water (2 × 50 mL), dried with sodium sulfate overnight, and filtered. After the removal of the solvent by a rotoevaporator, a clear, colorless liquid (5.33 g, 88.8%) was obtained. $^1$H NMR (500 MHz, CDCl$_3$): δ (ppm) 4.4 (t, 2H), 3.85 (t, 2H), 3.26 (s, 1H), 1.89 (s, 6H)

(3) Synthesis of 2-(phosphonooxy)ethyl 2-azido-2-methylpropanoate

2-azido-2-methyl-propionic acid 2-hydroxy-ethyl ester (2 g, 11.54 mmol) was dissolved in anhydrous THF (40 mL) in a 250 ml round-bottom flask. Anhydrous triethylamine (1.8 mL, 12.7 mmol) was added into the flask and mixture was cooled to 0 °C with an ice bath. The solution was stirred with magnetic stir bar. POCl$_3$ (1.2 mL, 12.7 mmol) was added
dropwise into the mixture. The reaction went for 5 hours and was quenched by adding DI water (40 mL). The solution was extracted with CH₂Cl₂ (3 × 35 mL), dried with sodium sulfate overnight, and filtered. After the removal of the solvent by a rotoevaporator and under vacuum overnight, a viscous, amber colored liquid (1.75 g, 60%) was obtained. ¹H NMR (500 MHz, CDCl₃): δ (ppm) 10.25 (br, 2H), 4.45 (br, 2H), 4.26 (br, 1H), 1.48 (s, 6H)