

Supporting Information

TiO₂ 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}

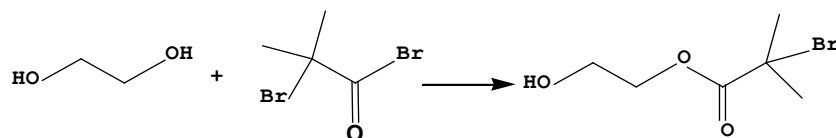
^a*Department of Materials Science and Engineering and Rensselaer Nanotechnology Center, Rensselaer Polytechnic Institute, Troy, New York 12180,*

^b*Department of Chemistry and Biochemistry and USC Nanocenter, University of South Carolina, Columbia, South Carolina 29208*

*to whom correspondence should be addressed: schadl@rpi.edu

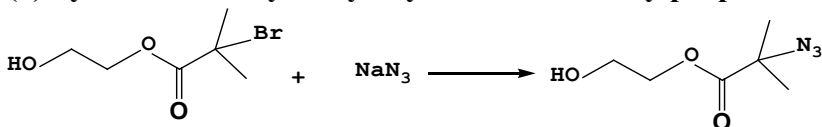
Synthesis of phosphate-azide ligand

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



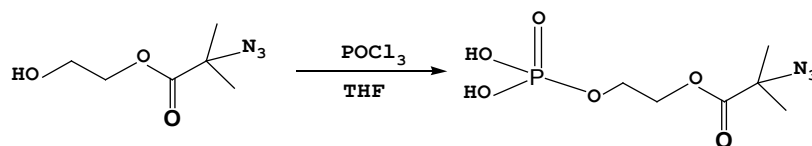
To a 250 mL round-bottom dry flask was added anhydrous ethylene glycol (55 mL, 1 mol). The flask was put into an ice bath and stirred with magnetic stir bar. And then 2-bromoisobutyl bromide (5 mL, 40 mmol) was added dropwise into the flask. The solution was stirred for 3 hours and quenched with 25 mL DI water. The solution was extracted with CH_2Cl_2 (3×25 mL), dried with sodium sulfate overnight, and filtered. After the removal of the solvent by a rotoevaporator, 2-bromo-2-methyl-propionic acid 2-hydroxyl ester was obtained as a colorless liquid (yield: 8.2 g, 82.5%). ^1H 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-2-methyl-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_2Cl_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. ^1H 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-(phosphonoxy)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)