Metallized hyperbranched polydiyne: a photonic material with a large refractive index tunability and a spin-coatable catalyst for facile fabrication of carbon nanotubes

*Matthias Häußler, Jacky Wing Yip Lam, Anjun Qin, Kalvin Ka Chun Tse, Martin Ka Shing Li, Jianzhao Liu, Cathy Ka Wai Jim, Ping Gao, and Ben Zhong Tang**

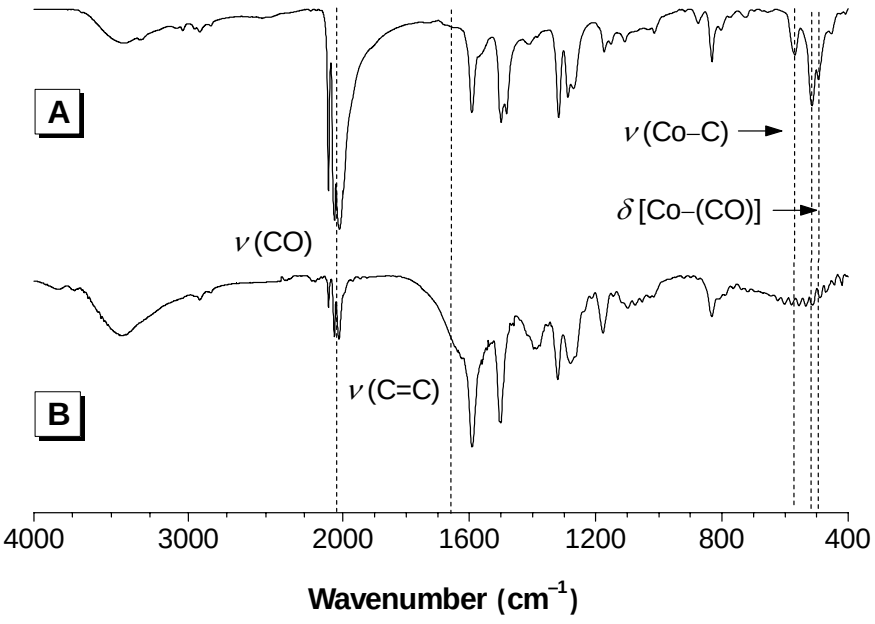

Figure S1. IR spectra of thin solid films of *hb*-PTEPA(Co) (A) before and (B) after UV photolysis.

Materials and Instrumentations. Octacarbonyldicobalt [$Co_2(CO)_8$] was purchased from Fluka and stored in a dark, cold, and dry place before use. Toluene was distilled over sodium benzophenone ketyl. *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA), *o*-dichlorobenzene (*o*-DCB) and other reagents and solvents were all purchased from Aldrich and used as received. Hyperbranched poly[tris(4-ethynyl-phenyl)amine] (*hb*-PTEPA) and its cobalt complex *hb*-PTEPA(Co) were prepared according to our previously published procedures.[1,2]

Thin films were prepared by spin-coating polymer solutions (~10 wt % in toluene) at 2000 rpm for 1 min on silicon wafers or glass substrates. The wafers and substrates were cleaned prior to use by sequential treatments for 10 min with dichloromethane, 2-propanol, piranha solution (30 vol % H_2O_2/ H_2SO_4), and deionized water in an ultrasonic bath. Refractive indexes were determined on a J A Woollam Variable Angle Ellipsometry System with a wavelength tunability from 300 to 1700 nm. To fit the acquired Ψ and Δ curves with the data obtained from the 3-layer optical model consisting of crystalline silicon substrate, 2-nm SiO_2 layer, and a uniform polymer film, the Levenberg–Marquardt regression algorithm was employed. The Cauchy dispersion law was applied to describe the polymer layer from visible to IR region.

Morphologies of the carbon nanotubes (CNTs) were imaged on a JEOL JSM-6060 scanning electron microscope (SEM) operating at an accelerating voltage of 15 kV. Structures of the nanotubes were investigated by high-resolution transmission electron microscopy JEOL 2010F TEM. Raman spectra were obtained from a Renishaw Micro Raman/Photoluminescence System RM3000 equipped with a 514.5 nm argon laser.

Photopattern Fabrication. Two-dimensional photonic pattern was prepared by UV irradiation of a spin-coated thin film of *hb*-PTEPA(Co) for 30 min using a copper-negative mask. An Oriel 66002 UV lamp operating at 90 W was used as the light source. The photoirradiated thin film was examined by an Olympus BX 60 POM optical microscope without going through a development process.

CNT Growth. Multiwalled CNTs were grown by a chemical vapor deposition process. The freshly prepared thin films of *hb*-PTEPA(Co) were dried in vacuum at room temperature for 2 h and then

placed in a tube furnace. The temperature was raised by 10 ºC/min under a flow of hydrogen/nitrogen mixture (50:50 by volume). Once the temperature reached 700 ºC, the samples were isothermally annealed for 30 min and the CNT growth was initiated by the introduction of a flow of acetylene gas. The CVD process was continued for 20 min. Afterwards the samples were cooled to room temperature under a steam of nitrogen.

References

1. M. Häussler, R. Zheng, J. W. Y. Lam, H. Tong, H. Dong and B. Z. Tang, *J. Phys. Chem. B*, 2004, **108**, 10645.
2. M. Häußler, J. W. Y. Lam, R. Zheng, H. Dong, H. Tong and B. Z. Tang, *J. Inorg. Organomet. Polym. Mat.*, 2005, **15**, 519.