

A cost effective and eco-friendly *one-pot* process for PC61BM synthesis under aerobic conditions

Rachana Kumar,* Samya Naqvi, Neha Gupta and Suresh Chand

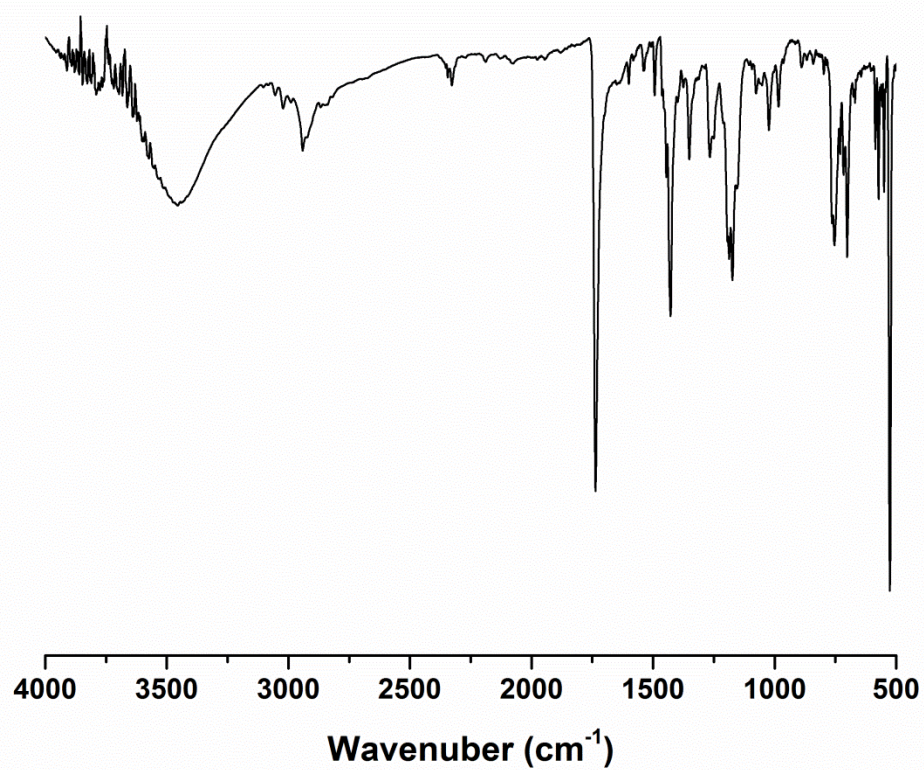
SUPPORTING INFORMATION

EXPERIMENTAL PROCEDURE

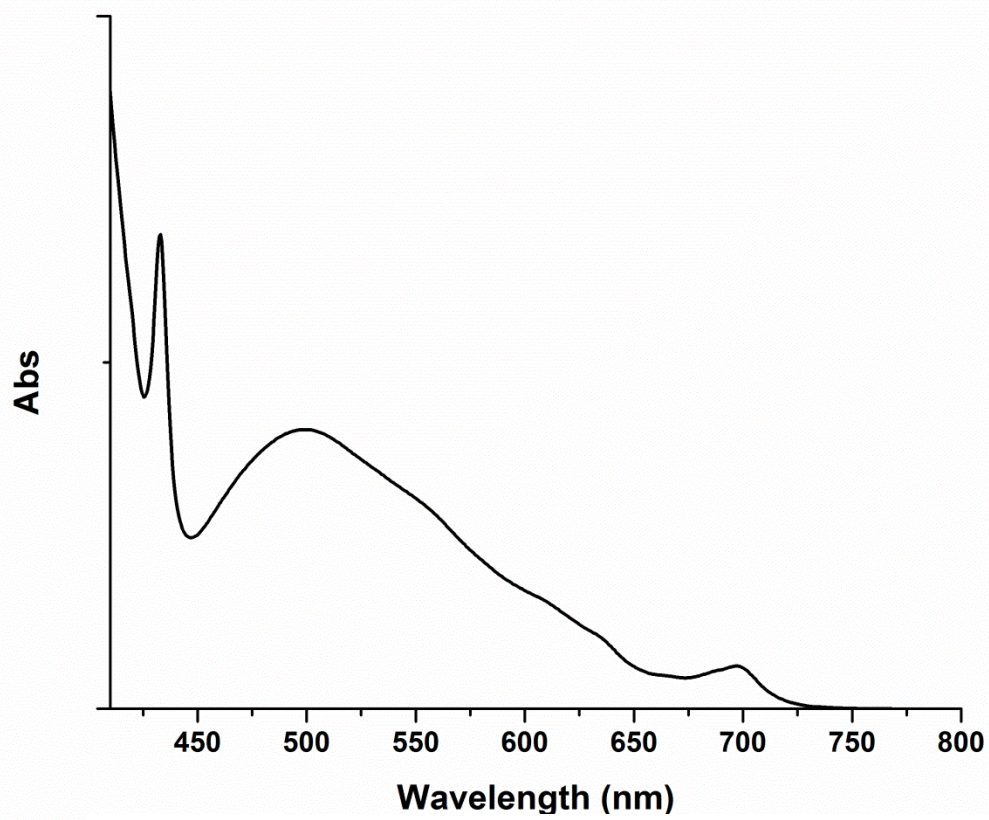
General method of Ester synthesis: 4-benzoyl butyric acid (5.2 mM) is dissolved in 50 mL methanol and ~2 mL acetic acid with a few drops of conc. Sulfuric acid is added. The temperature of the reaction mixture is raised to refluxing and progress of the reaction is monitored by running TLC in dichloromethane. After ~ 6 hr, reaction mixture is concentrated and product is purified by column chromatography using dichloromethane as solvent. Ester comes out as first fraction. Yield ~90%. FTIR (KBr) 1735, 1686 cm^{-1} .

General method of hydrazone synthesis: Ester (5.2 mM) and *p*-toluene sulfonyl hydrazide (1.2 eq) are dissolved in methanol (50 mL) and refluxed with stirring for ~6 hr followed by stirring at room temperature over night. Crystals of hydrazone come out on cooling and collected after washing with cold methanol. Yield ~99 %. FTIR (ν , cm^{-1}): 3111, 1712, 1371, 1228, 1172 cm^{-1} .

One pot synthesis of PCBM: Above hydrazone (0.14 mM or 1.4 mM) is dissolved in dichloromethane (10 mL or 20 mL) and cooled down to 0°C. ~0.7 mL (or 1.5 mL) triethyl amine is added and stirred for three hours at this temperature. A solution of C_{60} (0.3 eq) in *o*-dichlorobenzene is added and temperature is raised to 75-80 °C. Stirred at this temperature for 18 hours followed by precipitation with methanol. Solid is collected by centrifugation and loaded on column (200 mm x 18 mm or 1500 mm x 350 mm) for purification with toluene. Unreacted fullerene comes as first fraction followed by monoadduct ([5,6]PCBM, 40 % yield), a small fraction of bis/multi adduct is collected with ethyl acetate. [5,6]PCBM is converted in to [6,6] isomer by refluxing in *o*-DCB (20 mL) for ~ 5 hours (yield 100 %). FTIR (ν , cm^{-1}): 1737, 1445, 1428, 1187, 758, 698, 568, 547 and 527; UV-vis (DCM) (nm): 328, 430, 492 and 698. PCBM ^1H NMR (δ , CDCl_3): 7.85 (d, 2H, *o*-H Ph), 7.48 (t, 2H, *m*-H Ph), 7.37 (m, 1H, *p*-H Ph), 3.66 (s, 3H, OCH₃), 2.84 (t, 2H, PhCCH₂), 2.45 (t, 2H, CH₂COOR), 2.11 (q, 2H, CH₂CH₂COOR). ^{13}C NMR (δ , CDCl_3): 172.5 (CO₂Me), 32 peaks between 150-127, 78.8, 50.7, 32.9, 32.6, 21.3 ppm.

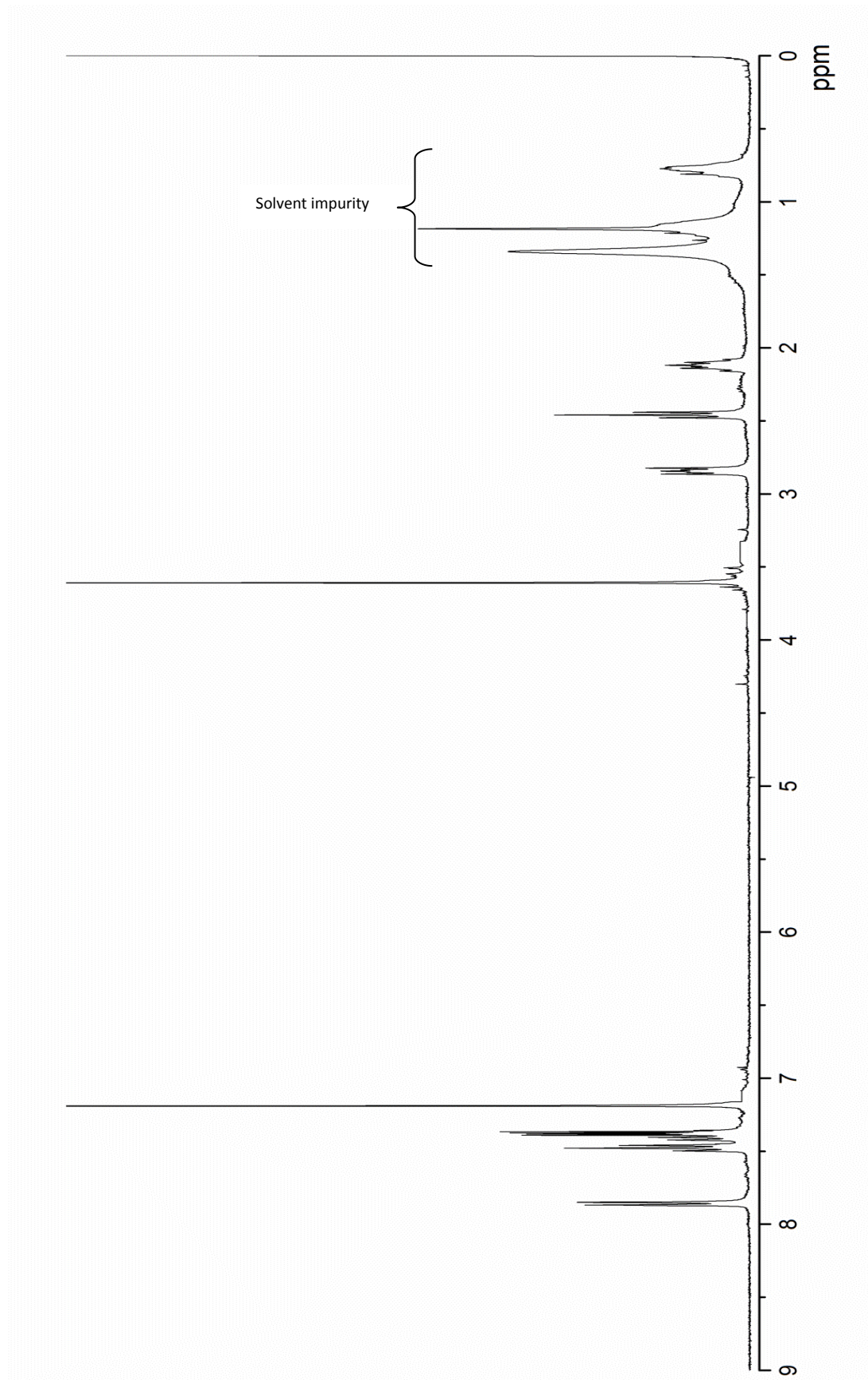


S1. FTIR of [6,6]PC61BM

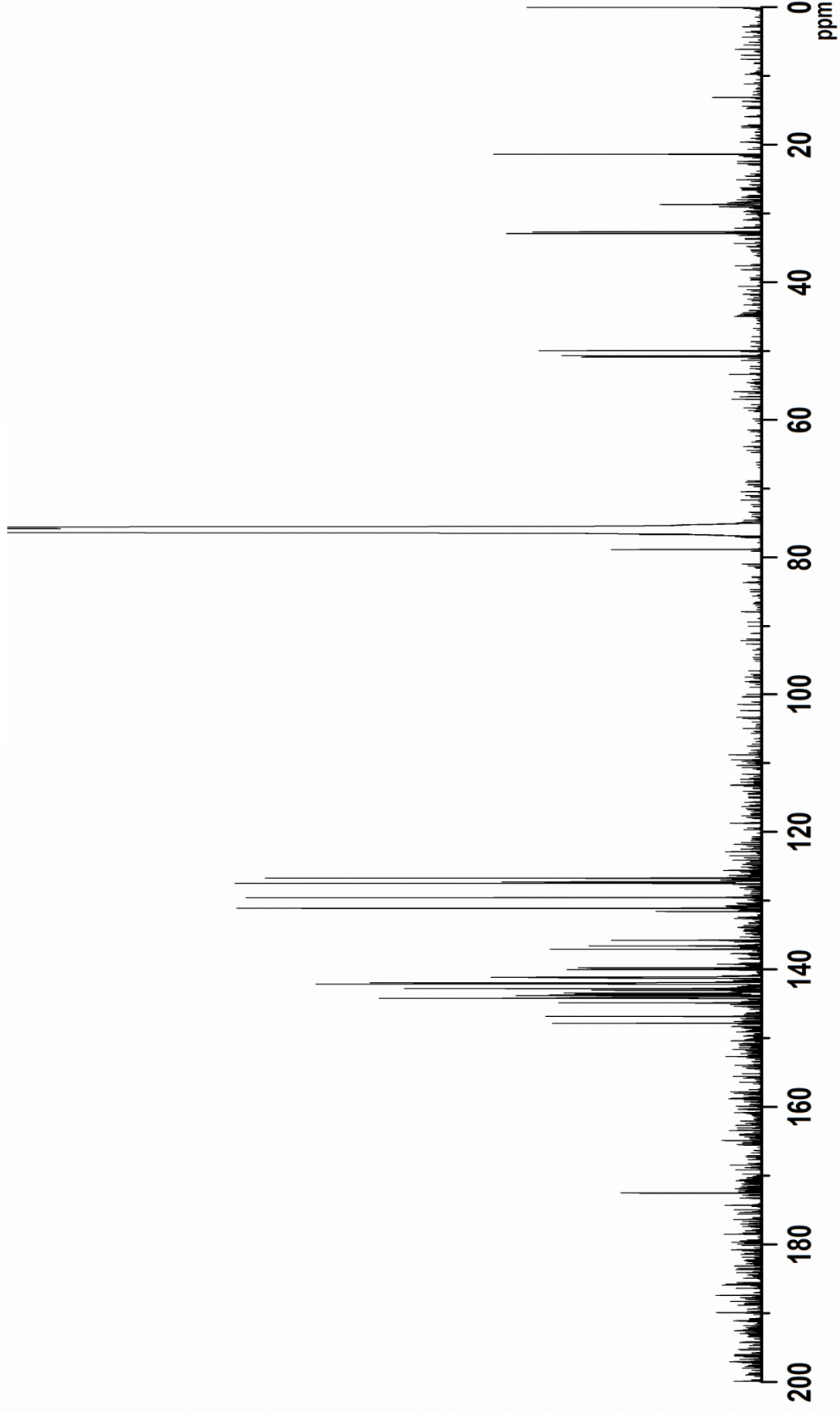


S2. UV-vis absorption spectrum of of [6,6]PC61BM in DCM.

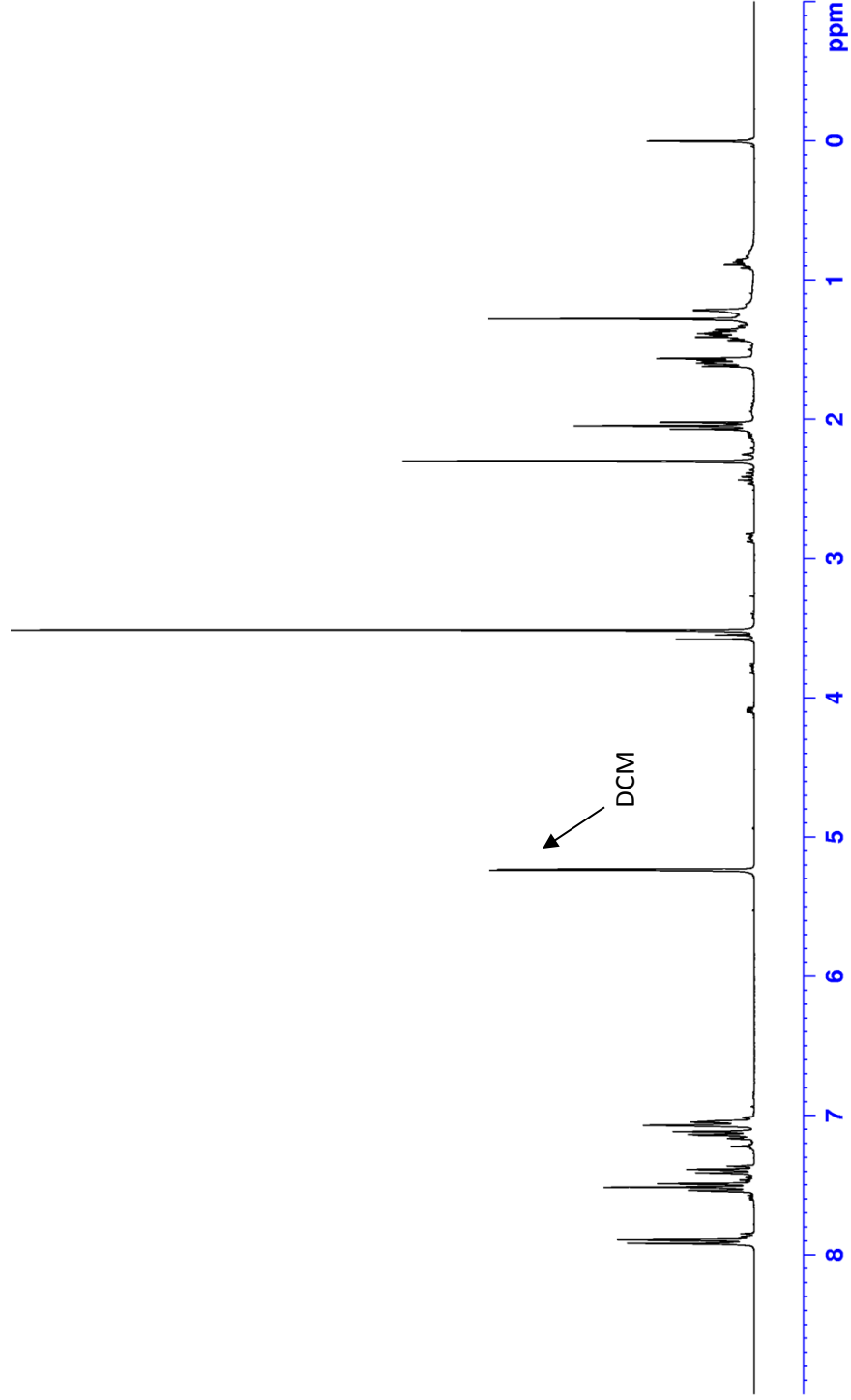
[6,6]PC61BM



[6,6]PC61BM



[5,6]PC61BM



[5,6]PC61BM

