Supplementary Information

Preparation and characterization of Polybenzoxazine/Polyhedral Oligomeric Silsesquioxane/SWCNTs Hybrid Complexes through Supramolecular Interactions

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Experimental Section

(3-(Pyren-1-yl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methanol (Py-Bz-OH)

A solution of 4-hydroxybenzyl alcohol (2.29 g, 18.4 mmol), pyren-1-amine (2.00 g, 9.20 mmol), and paraformaldehyde (1.38 g, 46 mmol) in dioxane/toluene/ethanol (8/8/4 mL) was heated in a 50-mL two-necked flask under N_2at 100 ºC for 12 h, and then the solvent was evaporated under reduced pressure. The solid residue was washed with CH_2Cl_2 and 1 M NaOH (aq.) and then dried ($MgSO_4$) The product was purified through column chromatography (SiO_2; *n*-hexane/THF, 1:1), yielding a yellow powder (78%). ^{1}H NMR (d_6-DMSO, ppm): 4.37 (d, 2H, ArC*H*$_2$OH), 4.80 (s, 2H, CHC*H*$_2$N), 5.49 (s, 2H, OC*H*$_2$N), 6.83 (d, 1H, CH$_2$OCC*H*CH), 7.02 (s, 1H, NCH$_2$CC*H*C), 7.12 (d, 1H, CH$_2$OCCHC*H*C), 7.88–8.38 (m, 9H, Py-*H*); ^{13}C NMR (d_6-DMSO, ppm): 52.18 (CH*C*H$_2$N), 62.84 (Ar*C*H$_2$OH), 82.07 (O*C*H$_2$N), 116.39–131.13 (aromatic), 135.52 (*C*CH$_2$OH), 144.02 (N*C*C(CH)), 153.80 (O*C*CH); FTIR (KBr, cm^{-1}): 942 (out-of-plane C–H bending from oxazine ring), 1240 (Ar–O–C stretching), 3394, 3566, 3628 (Ar–OH stretching).

(3-(Pyren-1-yl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl Acrylate (Py-Bz-Ac)

Py-Bz-OH (1.50 g, 4.10 mmol) and Et_3N (1.25 g, 12.3 mmol) were placed in THF (20 mL) in a 50-mL two-necked flask under N_2 and cooled in an ice bath for 30 min. Acryloyl chloride (1.11 g, 12.3 mmol) was added and then the mixture was stirred for 3 h at room temperature. The reaction was quenched with 1 M $NaHCO_3$ and partitioned between distilled water and CH_2Cl_2. The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified through column chromatography (SiO_2; *n*-hexane/THF, 4:1), yielding a yellow product (70%).^{1}H NMR (d_6-DMSO, ppm): 4.80 (s, 2H,

CHC*H*$_2$N), 5.02 (s, 2H, ArC*H*$_2$OC=O), 5.54 (s, 2H, OC*H*$_2$N), 5.88, (d, 1H, CCH=C*H*$_2$), 6.16 (dd, 1H, CC*H*=CH$_2$), 6.35 (d, 1H, CCH=C*H*$_2$), 6.83 (d, 1H, CH$_2$OCC*H*CH), 7.02 (s, 1H, NCH$_2$CC*H*C), 7.11 (d, 1H, CH$_2$OCCHC*H*C), 7.88–8.38 (m, 9H, Py-*H*); ^{13}C NMR (d_6-DMSO, ppm): 52.18 (CH*C*H$_2$N), 65.2 (Ar*C*H$_2$OC=O), 82.07 (O*C*H$_2$N), 127.85 (CH=*C*H$_2$), 132.50 (C*C*H=CH$_2$), 117.06–132.43 (aromatic), 144.51 [N*C*C(CH)], 154.53 (CH*C*OC*H*$_2$N), 166.19 (*C*=O); FTIR (KBr, cm^{-1}): 942 (out-of-plane C–H bending from oxazine ring), 1180 (C–O–C stretching), 1722 (C=O stretching).

(3-(Pyren-1-yl)-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazin-6-yl)methyl3-(5-Methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)propanoate (Py-Bz-T)

A solution of T (1.68 g, 13.3 mmol) and Et$_3$N (1.35 g, 13.3 mmol) in DMSO (20 mL) was heated in a 50-mL two-necked flask under N$_2$ at 55 ºC for 2 h. The solution was injected into a two-necked flask under N$_2$ containing Py-Bz-Ac (1.4 g, 3.34 mmol) and then the mixture was heated at 55 ºC for 24 h. The solvent was evaporated under reduced pressure. The residue was washed with CH$_2$Cl$_2$ and then the solution was filtered to remove any unreacted T. Re-precipitation from EtOH yielded a yellow powder (58%). ^{1}H NMR (d_6-DMSO, ppm): 1.67 (s, 3H, NCH=CC*H*$_3$), 2.67 (d, 2H, O=CC*H*$_2$CH$_2$N), 3.83 (d, 2H, O=CCH$_2$C*H*$_2$N), 4.83 (s, 2H, CHC*H*$_2$N), 4.93 (s, 2H, ArC*H*$_2$OC=O), 5.54 (s, 2H, OC*H*$_2$N), 6.87 (d, 1H, CH$_2$OCC*H*CH), 7.08 (s, 1H, NCH$_2$CC*H*C), 7.14 (d, 1H, CH$_2$OCCHC*H*C), 7.43 (s, 1H, O=CNC*H*=C) 7.88–8.38 (m, 9H, Py-*H*), 11.22 (1H, O=CN*H*C=O); ^{13}C NMR (d_6-DMSO, ppm): 11.96 (NCH=C*C*H$_3$), 32.92 (O=C*C*H$_2$CH$_2$N), 43.95 (O=CCH$_2$*C*H$_2$N), 52.18 (CH*C*H$_2$N), 65.99 (Ar*C*H$_2$OC=O), 82.14 (O*C*H$_2$N), 108.70 (NCH=*C*CH$_3$), 115.91–135.65 (aromatic), 142.43 (N*C*H=C), 144.49 [N*C*C(CH)], 151.53 (N*C*=ONH), 154.49 (CH*C*OC*H*$_2$N), 165.08 (O*C*=O), 171.52 (NH*C*=OC); FTIR (KBr, cm^{-1}): 942 (out-of-plane C–H bending of oxazine ring), 1240 (Ar–O–C stretching), 1676 (C=O stretching), 3186 (NH stretching).

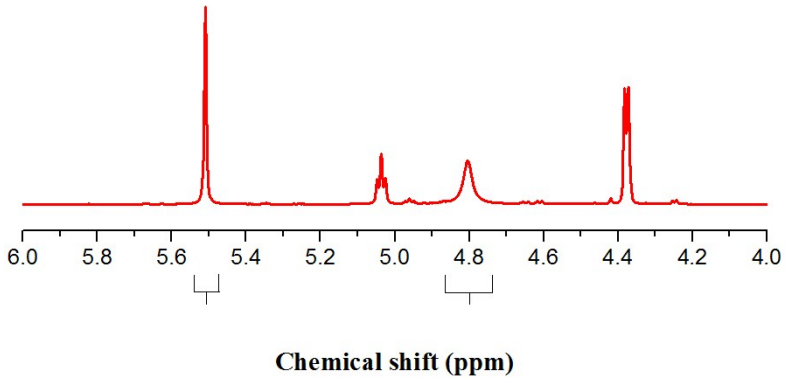


Fig. S1 ^{1}H NMR spectrum of Py-Bz-OH.

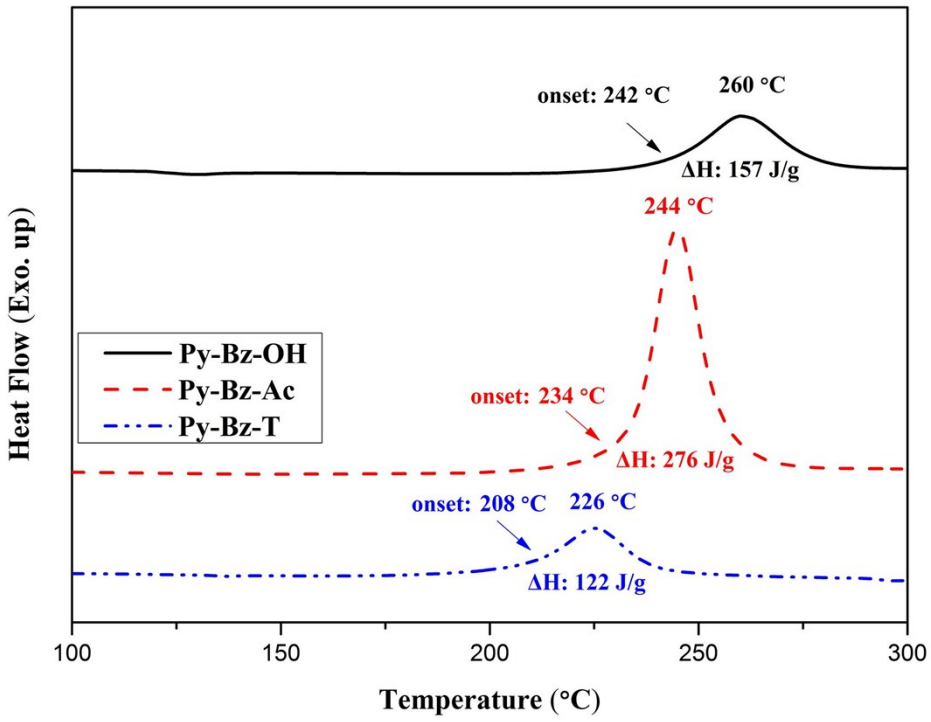
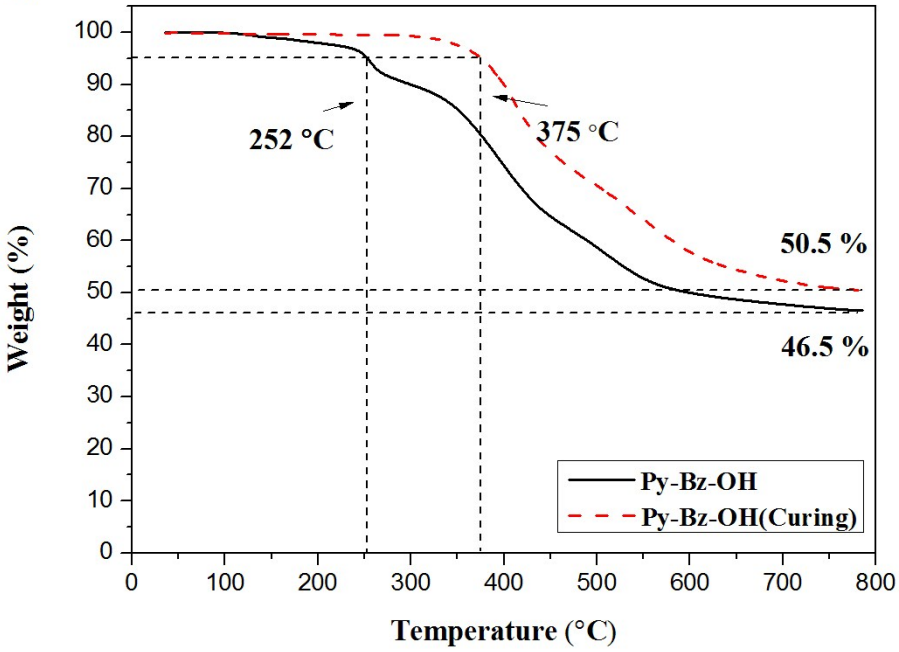
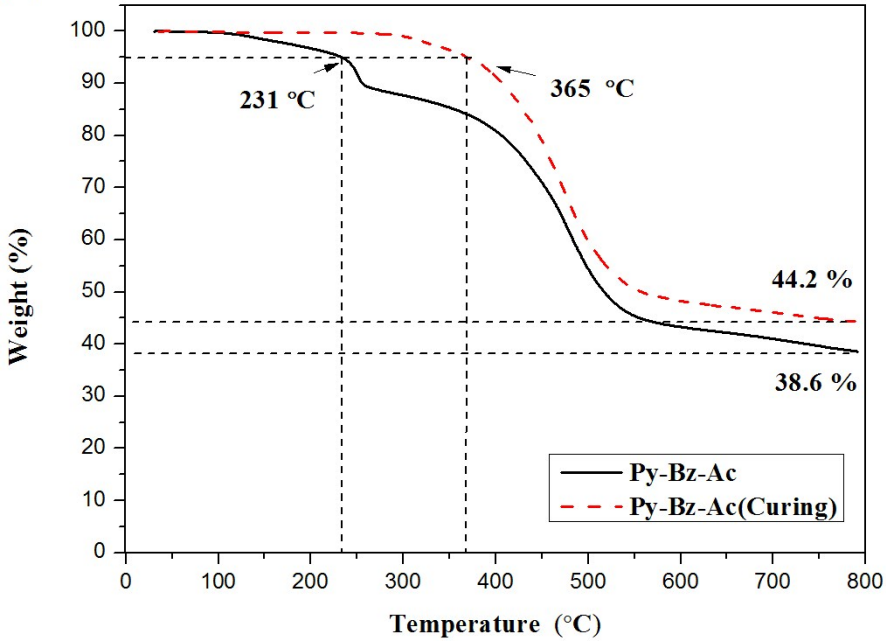


Fig. S2 DSC thermograms of Py-Bz-OH, Py-Bz-Ac, and Py-Bz-T.

(a)


Weight (%)
Temperature (°C)
252 °C
375 °C
50.5 %
46.5 %
Py-Bz-OH
Py-Bz-OH(Curing)

(b)


Weight (%)
Temperature (°C)
231 °C
365 °C
44.2 %
38.6 %
Py-Bz-Ac
Py-Bz-Ac(Curing)

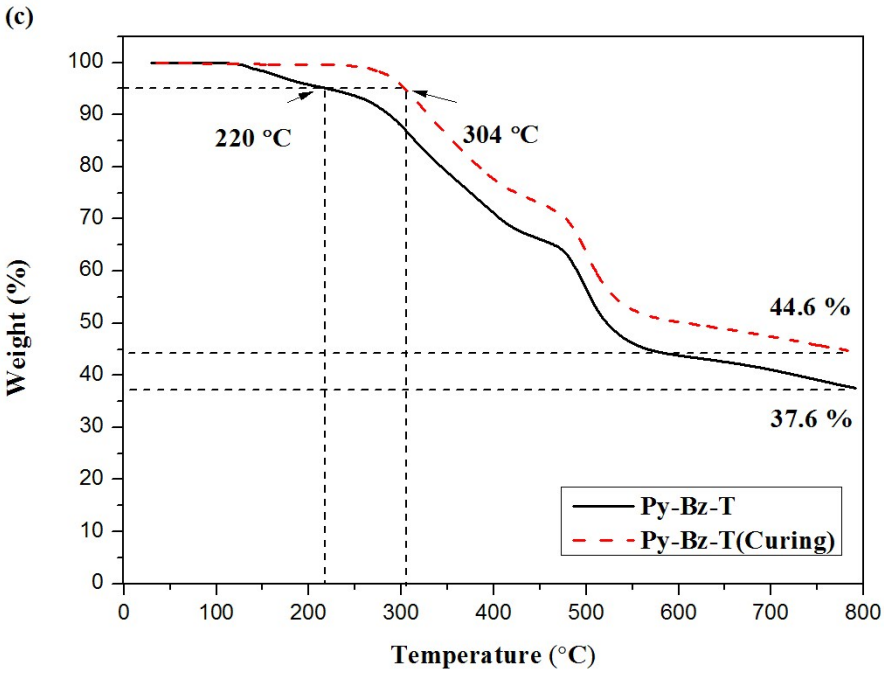


Fig. S3 TGA traces of (a) Py-Bz-OH and cured Py-Bz-OH; (b) Py-Bz-Ac and cured Py-Bz-Ac; (c) Py-Bz-T and cured Py-Bz-T.

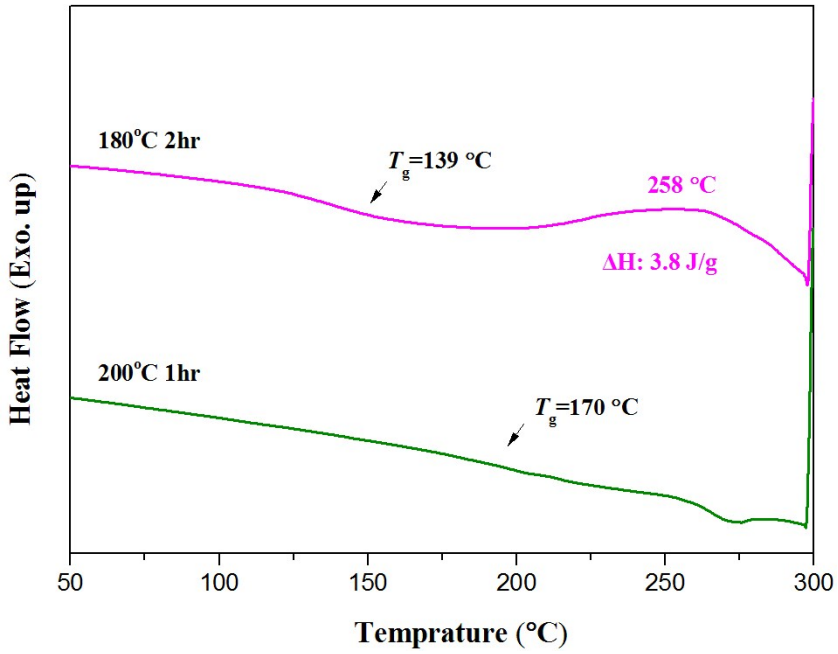
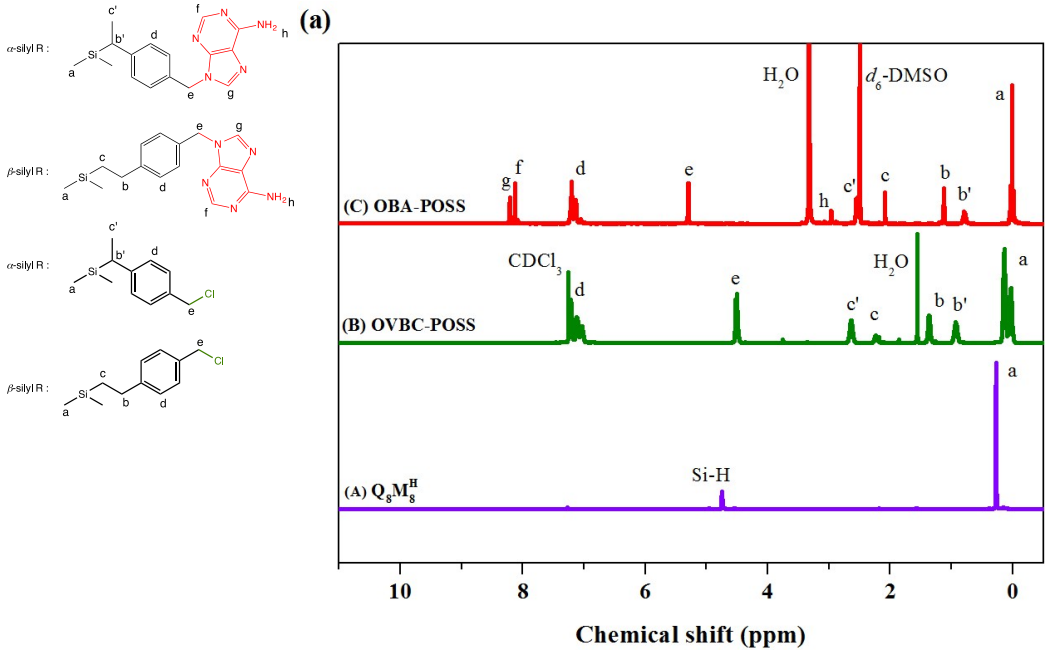
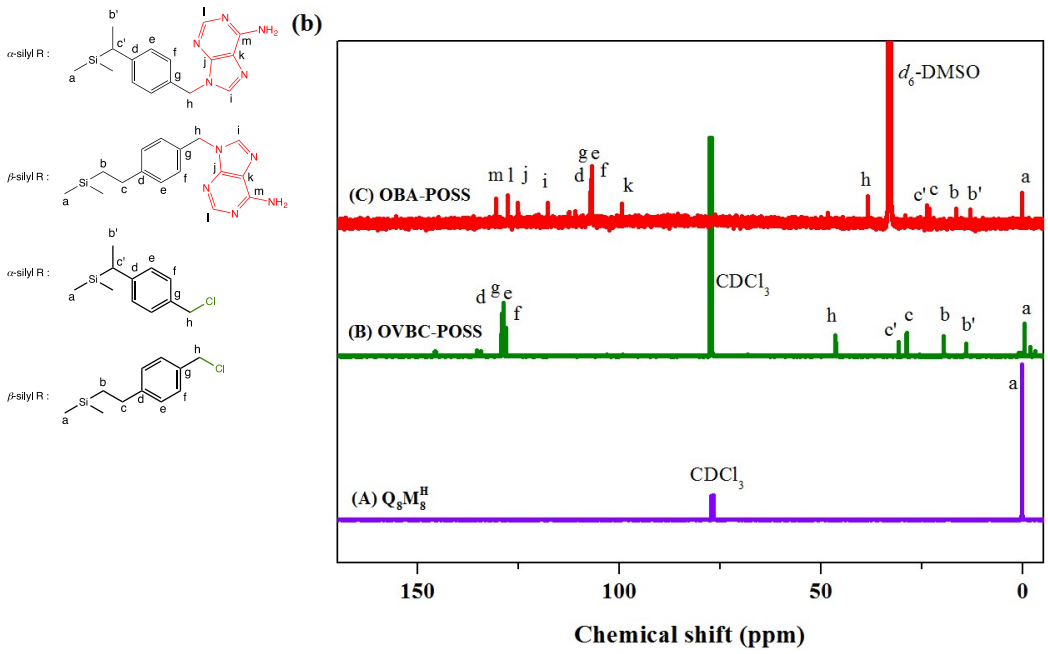


Fig. S4 DSC thermograms of of Py-Bz-T, recorded after 180 ºC 2 h, and 200 ºC 1 h.


(a)
α-silyl R :
β-silyl R :
α-silyl R :
β-silyl R :
(C) OBA-POSS
(B) OVBC-POSS
(A) $Q_8M_8^H$
H_2O
d_6-DMSO
$CDCl_3$
Si-H
Chemical shift (ppm)


(b)
α-silyl R :
β-silyl R :
α-silyl R :
β-silyl R :
(C) OBA-POSS
(B) OVBC-POSS
(A) $Q_8M_8^H$
d_6-DMSO
$CDCl_3$
Chemical shift (ppm)

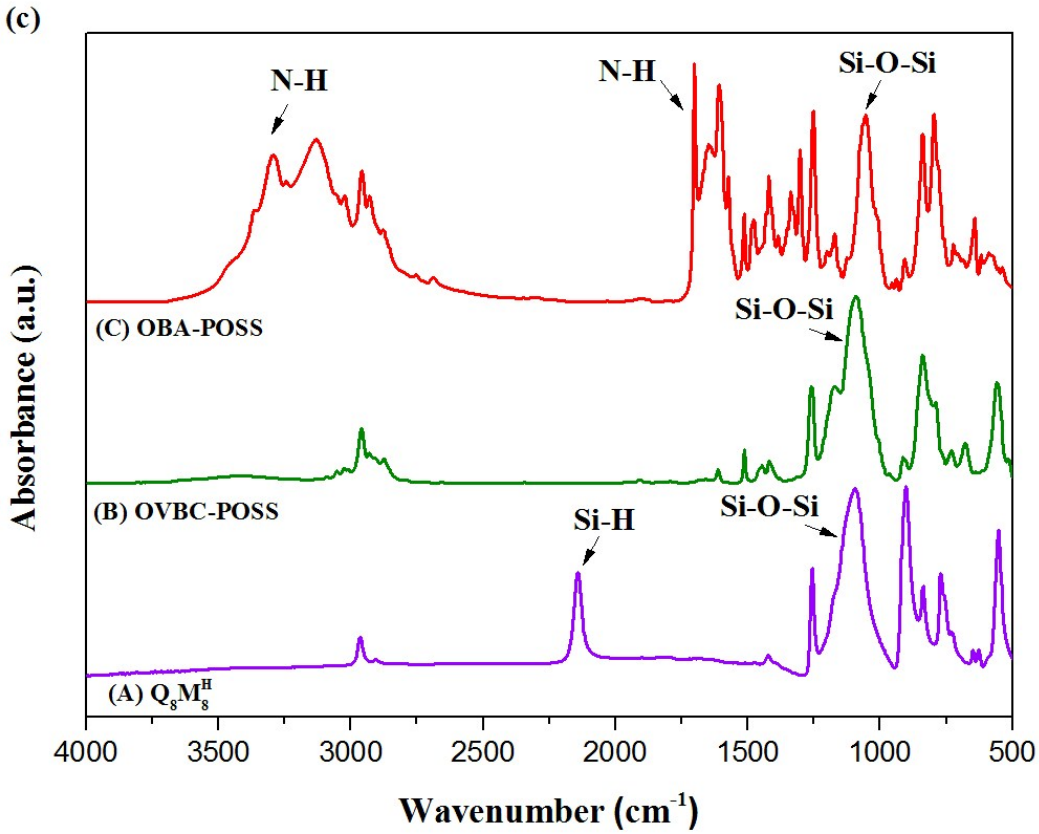


Fig. S5 (a) ^{1}H NMR spectra, (b) ^{13}C NMR spectra, and (c) FTIR spectra of Q_8M_8, OVBC-POSS, and OBA-POSS.

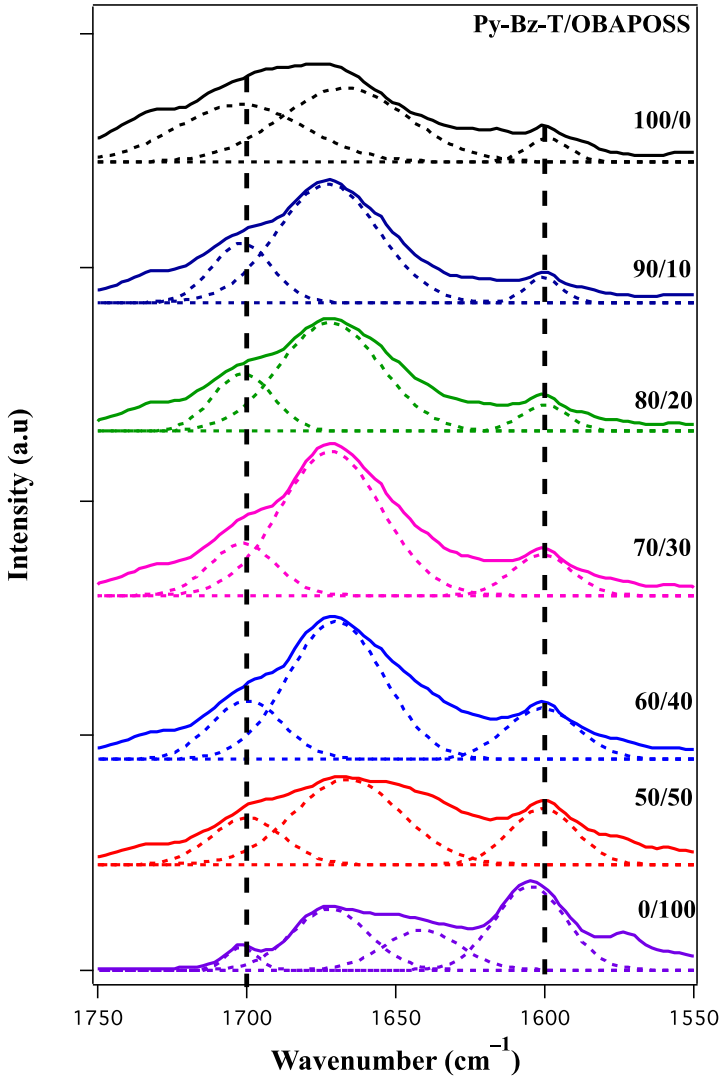


Fig. S6 FTIR spectra and fitting results with different wt% of Py-Bz-T/OBA- POSS nanocomposite at 1750-1550 cm^{-1} region.

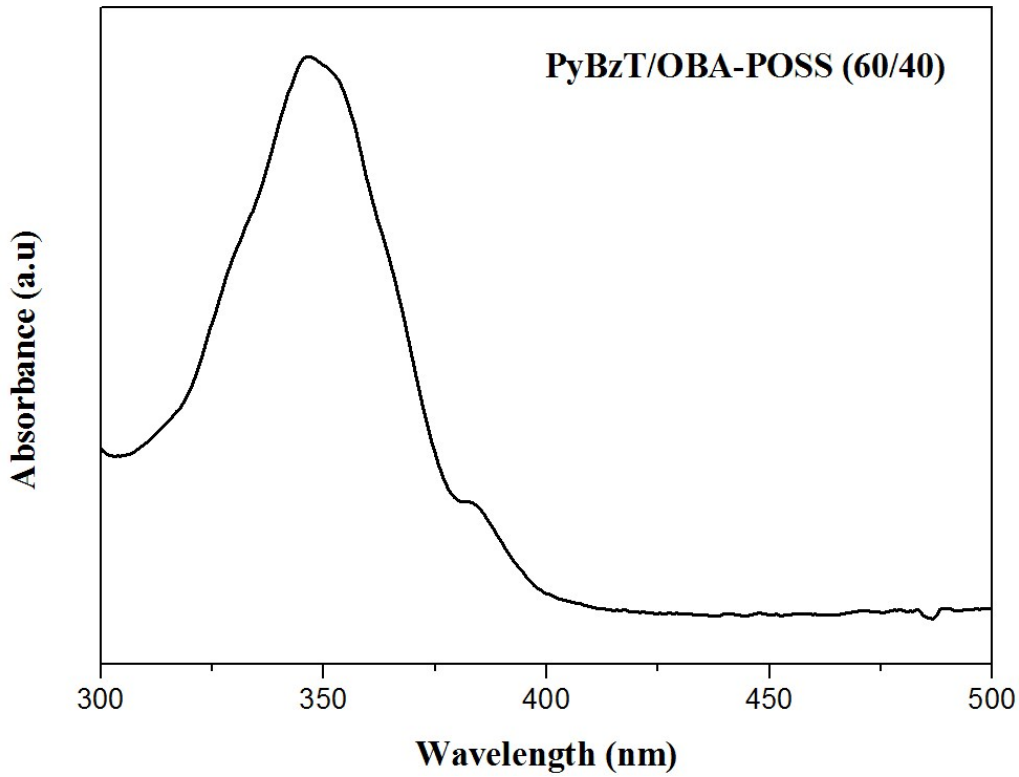


Fig. S7 UV-vis spectrum of Py-Bz-T/OBA-POSS nanocomposite (60/40).