

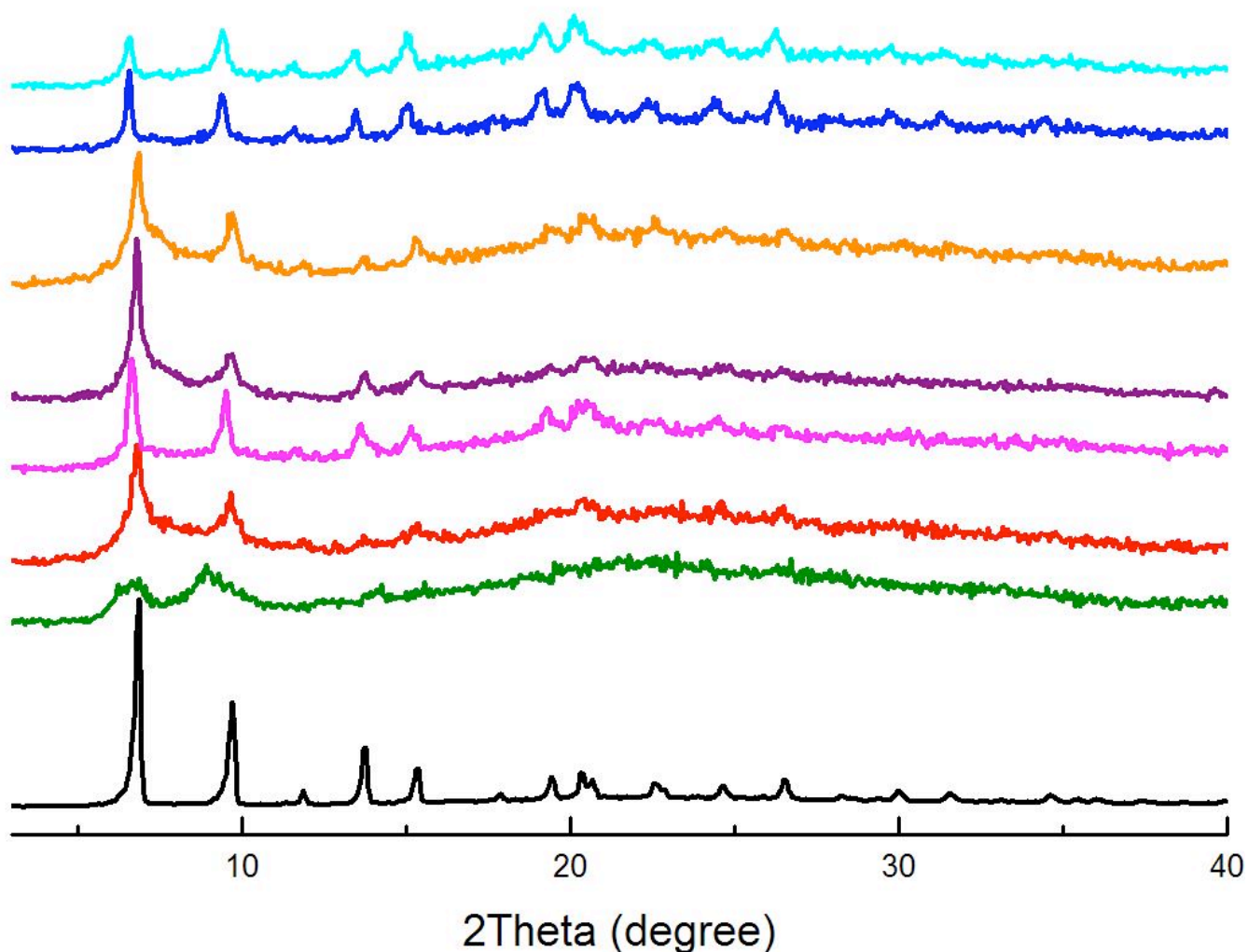
# Covalent Modification of a Metal-Organic Framework with Iso cyanates: Probing Substrate Scope and Reactivity

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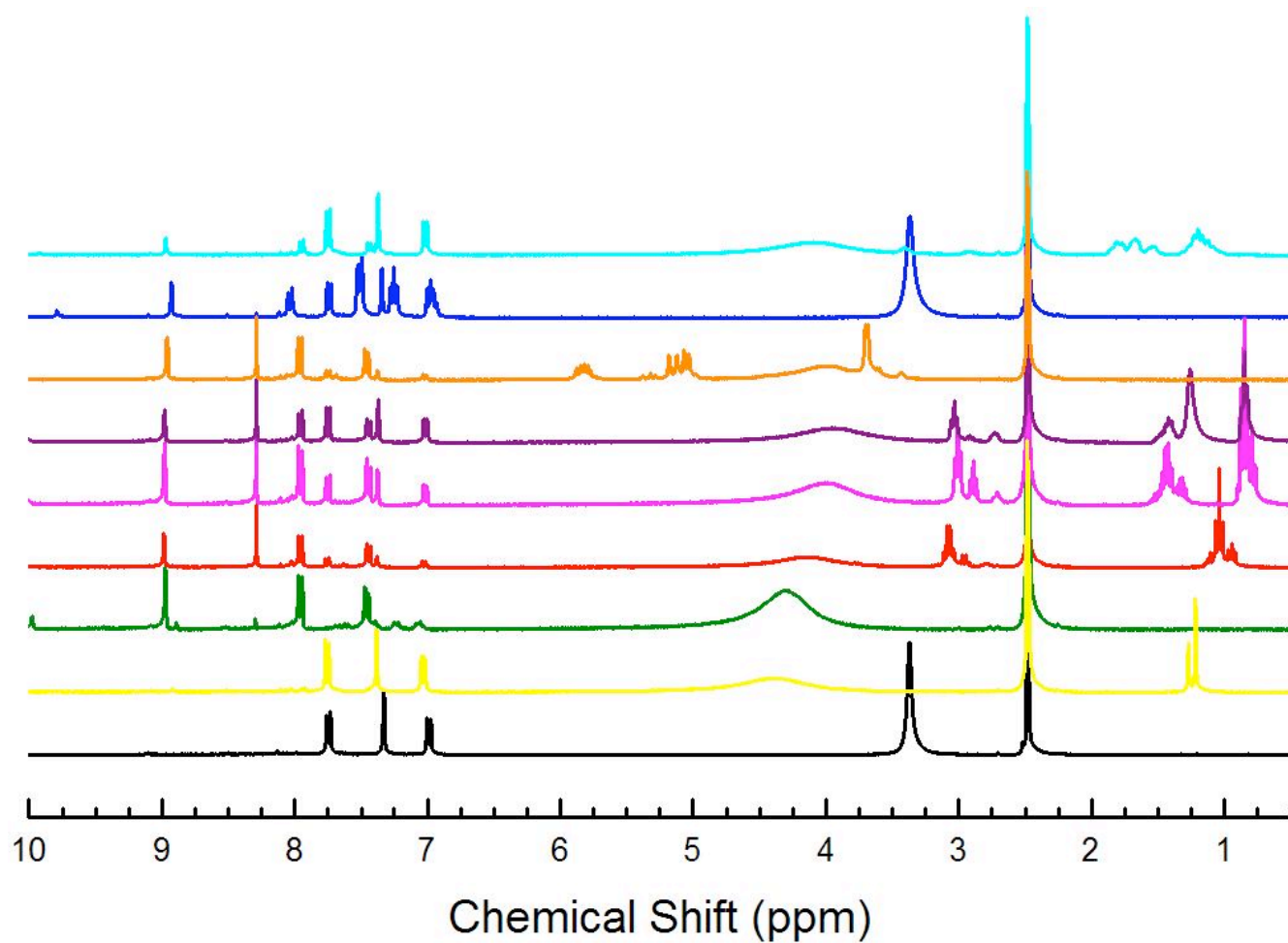
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## ELECTRONIC SUPPLEMENTARY INFORMATION

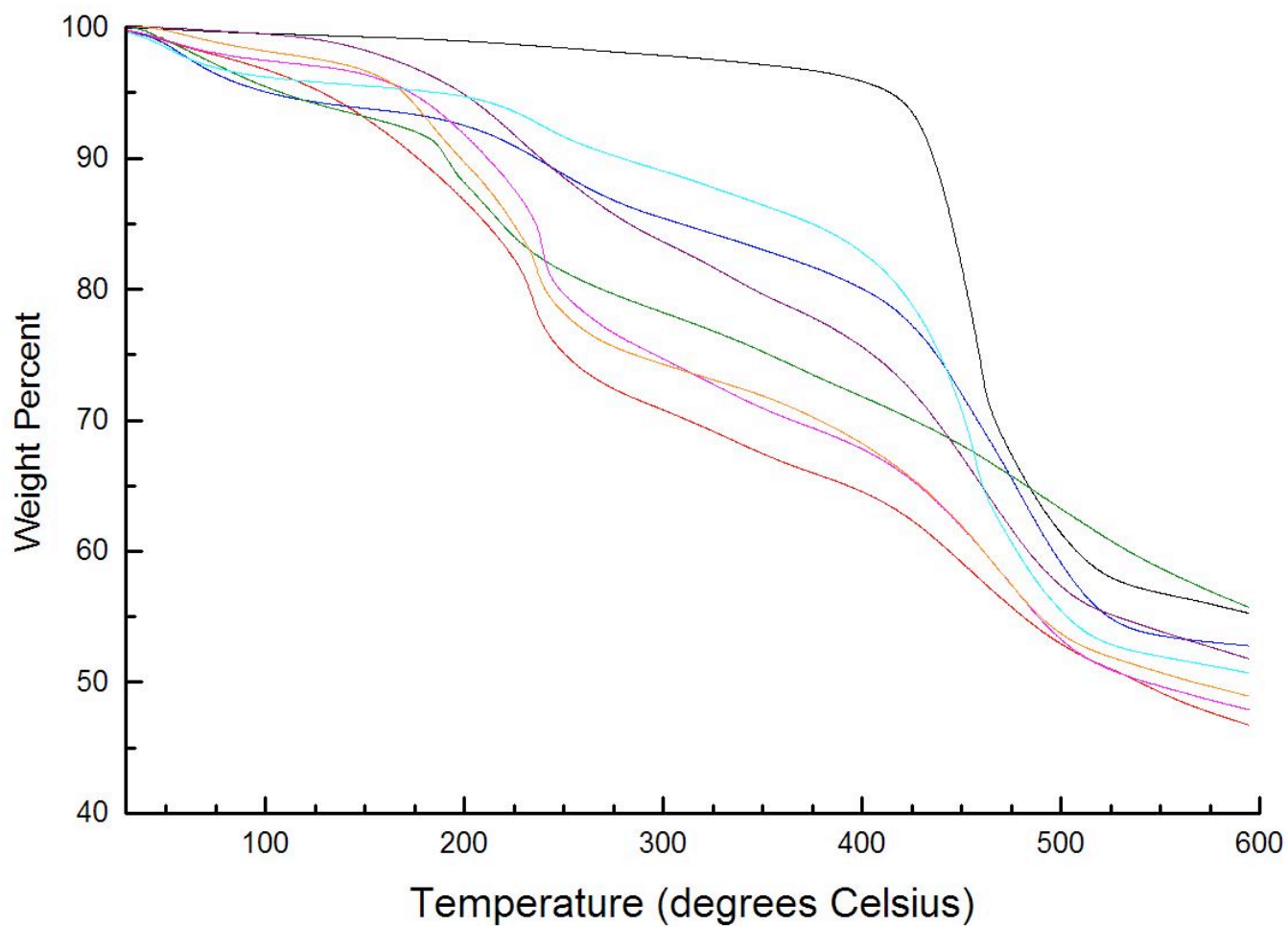
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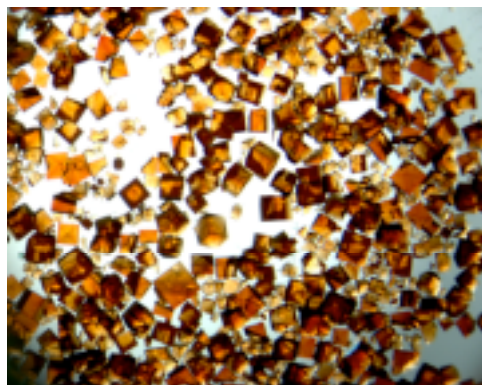
**Figure S1.** Comparison of PXRD patterns (all solvent exchanged with  $\text{CHCl}_3$  unless noted otherwise) from as-synthesized IRMOF-3 (black, prepared from DMF), IRMOF-3-UR0 (green), IRMOF-3-UR2 (red), IRMOF-3-UR3 (pink). IRMOF-3-UR5 (purple), IRMOF-3-URAl (orange), IRMOF-3-URPh (blue), and IRMOF-3-URCy (cyan). Samples were soaked and washed with fresh  $\text{CHCl}_3$  for 3 days after the reaction with isocyanate. The solvent was decanted and the samples were left drying in air prior to PXRD analysis.



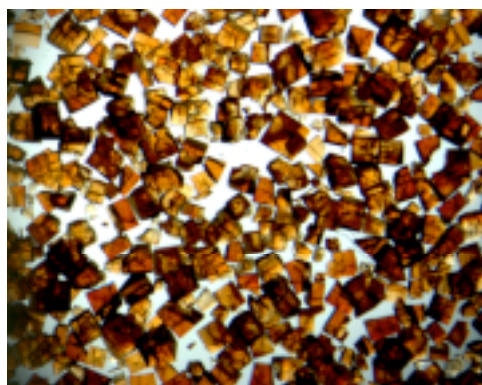
**Figure S2.**  $^1\text{H}$  NMR spectra of digested samples of: IRMOF-3 (black, no isocyanate), IRMOF-3 (yellow, exposed to *t*-butylisocyanate), IRMOF-3-UR0 (green), IRMOF-3-UR2 (red), IRMOF-3-UR3 (pink), IRMOF-3-UR5 (purple), IRMOF-3-URAl (orange), IRMOF-3-URPh (blue), and IRMOF-3-URCy (cyan),



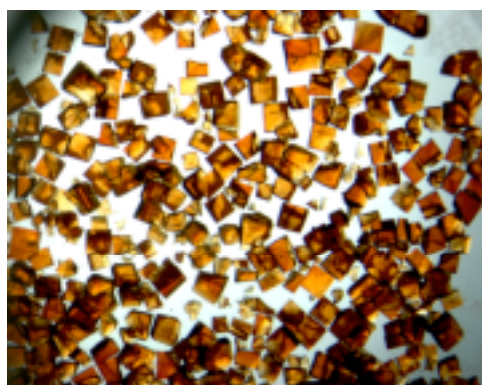
**Figure S3.** Thermogravimetric analysis (TGA) of modified IRMOF-3 samples. All samples were previously dried at 80 °C under vacuum for 4-5 h. Modified IRMOF-3 (10-12 mg) was heated at a scan rate of 10 °C/min from 30 °C to 600 °C. IRMOF-3 (black), IRMOF-3-UR0 (green), IRMOF-3-UR2 (red), IRMOF-3-UR3 (pink). IRMOF-3-UR5 (purple), IRMOF-3-URAl (orange), IRMOF-3-URPh (blue), and IRMOF-3-URCy (cyan).



**Figure S4.** Crystals of IRMOF-3 after modification with tri(methylsilyl)isocyanate (IRMOF-3-UR0).



**Figure S5.** Crystals of IRMOF-3 after modification with propylisocyanate (IRMOF-3-UR3).



**Figure S6.** Crystals of IRMOF-3 after modification with allylisocyanate (IRMOF-3-URAl).

**Table S1.** Dinitrogen adsorption data at 77 K for IRMOF-3-UR2.

| Relative Pressure<br>( $P/P_o$ ) | Quantity Adsorbed<br>(cm <sup>3</sup> /g STP) | Relative Pressure<br>( $P/P_o$ ) | Quantity Adsorbed<br>(cm <sup>3</sup> /g STP) | Relative Pressure<br>( $P/P_o$ ) | Quantity Adsorbed<br>(cm <sup>3</sup> /g STP) |
|----------------------------------|-----------------------------------------------|----------------------------------|-----------------------------------------------|----------------------------------|-----------------------------------------------|
| 6.26E-06                         | 11.62662                                      | 0.252307191                      | 387.0539                                      | 0.875789903                      | 444.3958                                      |
| 8.38E-06                         | 23.24548                                      | 0.302443547                      | 393.5172                                      | 0.86018055                       | 444.2443                                      |
| 1.39E-05                         | 34.81849                                      | 0.351528992                      | 399.6771                                      | 0.840364155                      | 444.0453                                      |
| 2.16E-05                         | 46.33725                                      | 0.400293269                      | 405.7242                                      | 0.820181546                      | 443.9167                                      |
| 3.23E-05                         | 57.76482                                      | 0.450406926                      | 411.7357                                      | 0.800216215                      | 443.7496                                      |
| 4.70E-05                         | 69.0827                                       | 0.500231681                      | 417.844                                       | 0.770181985                      | 443.4638                                      |
| 6.71E-05                         | 80.2427                                       | 0.550421863                      | 424.0123                                      | 0.74021505                       | 443.0982                                      |
| 9.44E-05                         | 91.18705                                      | 0.600566566                      | 429.6046                                      | 0.700257874                      | 442.5407                                      |
| 0.000130064                      | 101.8515                                      | 0.650393559                      | 434.3194                                      | 0.650171111                      | 441.7294                                      |
| 0.000174816                      | 112.1805                                      | 0.70061746                       | 437.3785                                      | 0.60029788                       | 440.8781                                      |
| 0.000228499                      | 122.0955                                      | 0.740306774                      | 438.8256                                      | 0.550249238                      | 439.9041                                      |
| 0.000290308                      | 131.549                                       | 0.770364373                      | 439.5281                                      | 0.528050673                      | 439.395                                       |
| 0.000358872                      | 140.491                                       | 0.800442101                      | 440.0488                                      | 0.505856056                      | 438.8467                                      |
| 0.00046255                       | 151.8082                                      | 0.820449916                      | 440.4219                                      | 0.483982321                      | 436.8016                                      |
| 0.000580226                      | 163.0071                                      | 0.840439705                      | 440.8539                                      | 0.461154324                      | 434.5743                                      |
| 0.000713322                      | 174.4463                                      | 0.860473725                      | 441.1171                                      | 0.440848608                      | 426.0312                                      |
| 0.000862864                      | 185.8452                                      | 0.875403384                      | 441.3627                                      | 0.416861077                      | 413.3283                                      |
| 0.001029723                      | 197.2016                                      | 0.890574721                      | 441.5518                                      | 0.392867462                      | 406.4078                                      |
| 0.001221328                      | 208.4945                                      | 0.900468758                      | 441.782                                       | 0.373271651                      | 403.3162                                      |
| 0.001439747                      | 219.7208                                      | 0.907454357                      | 441.7427                                      | 0.350962511                      | 400.3836                                      |
| 0.001699256                      | 230.8413                                      | 0.932788323                      | 442.2977                                      | 0.300763523                      | 394.1013                                      |
| 0.002016298                      | 241.8122                                      | 0.934644692                      | 442.5254                                      | 0.250367686                      | 387.5054                                      |
| 0.002407108                      | 252.5818                                      | 0.941540535                      | 442.743                                       | 0.200220096                      | 380.7251                                      |
| 0.002891549                      | 263.092                                       | 0.966535936                      | 444.0589                                      | 0.150493554                      | 373.0681                                      |
| 0.003510842                      | 273.2073                                      | 0.968538122                      | 444.4368                                      |                                  |                                               |
| 0.00430436                       | 282.7804                                      | 0.975676484                      | 445.1914                                      |                                  |                                               |
| 0.004869374                      | 288.043                                       | 0.981891801                      | 445.9983                                      |                                  |                                               |
| 0.011578391                      | 315.5329                                      | 0.988981372                      | 446.6412                                      |                                  |                                               |
| 0.028893292                      | 336.2153                                      | 0.995726044                      | 447.2555                                      |                                  |                                               |
| 0.06446635                       | 352.9683                                      | 0.970439384                      | 446.4222                                      |                                  |                                               |
| 0.080723598                      | 357.8286                                      | 0.950005633                      | 445.7296                                      |                                  |                                               |
| 0.100766551                      | 362.856                                       | 0.929548362                      | 445.1801                                      |                                  |                                               |
| 0.140203741                      | 370.6446                                      | 0.909218377                      | 444.8409                                      |                                  |                                               |
| 0.200962595                      | 380.0943                                      | 0.888688351                      | 444.6287                                      |                                  |                                               |