# Function-Structure Relationship in Metal-Organic Frameworks for Mild, Green and Fast Catalytic C-C Bond Formation

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## Section 1. Linker exchange procedure.

## S1.1. Solvent assisted linker exchange (SALE) for TMU-4 to TMU-34.

A number of 10 ml screw cap glass vial was used for SALE procedure. 0.3 g activated TMU-4 added to each one of glass vials and followed by addition of 10 ml H<sub>2</sub>DPT ligand solution which had been prepared by dissolvation of 1 g H<sub>2</sub>DPT in 100 mL of DMF (10 g.L<sup>-1</sup> ligand solution). Sampling for monitoring the exchange process was carried out at 24 and 48 hours. Exchange procedure monitored photoluminescence spectroscopy techniques using PerkinElmer LS-55 fluorescence spectrometer.

PL experiments show that by increasing the time from 0 to 24 and then 48 hour, the emission peak of TMU-34 is enhancing (excitation wavelength: 482 nm, emission wavelength: 615.5 nm). This is clearly based on replacement of  $H_2DPT$  linker inside the pores of TMU-4. **Table S1** represents the results of linker exchange procedure.

 Table S1. Time-dependent exchange percentage by PL method.

Time (hour)	Exchange Progress
0	0%
24	50%
48	95%

These data for exchange progress (%) are calculated by equation (1):

Exchange progress (%) =  $[(I_{615.5}^{t})/(I_{615.5}^{TMU-34})]*100$  (1)

Where  $I_{615.5}$ <sup>t</sup> is maximum emission wavelength in the emission spectrum of (X%-H<sub>2</sub>DPT)-TMU-4 at time t up on excitation at 482 nm and  $I_{615.5}$ <sup>TMU-34</sup> is maximum emission wavelength in the emission spectrum of TMU-34. Here, the name of (X%-H<sub>2</sub>DPT)-TMU-4 represent the percentage (X%) of exchanged BPDB linkers inside the TMU-4 framework with H<sub>2</sub>DPT linkers to synthesis frameworks with different ratios of H<sub>2</sub>DPT linker to approve the effect of functional linker on the Knoevenagel condensation.

For TMU-4, (50%-H<sub>2</sub>DPT)-TMU-4, (95%-H<sub>2</sub>DPT)-TMU-4 and TMU-34 framework, there are 0%, 50%, 95% and 100% of H<sub>2</sub>DPT pillar spacer in the framework. The results of GC analysis

(**Table S2**) show that after exchange reaction, by increasing the percentage of  $H_2DPT$  ligand, the reaction conversion at 60 min is increased.

**Table S2.** Results of Knoevenagel condensation by TMU-4,  $(50\%-H_2DPT)$ -TMU-4,  $(95\%-H_2DPT)$ -TMU-4 and TMU-34 frameworks after 60 min.

TMU-Framework	Reaction conversion
TMU-4	45%
(50%-H <sub>2</sub> DPT)-TMU-4	79%
(95%-H <sub>2</sub> DPT)-TMU-4	97%
TMU-34	>99 %

### S1.2. Solvent assisted linker exchange (SALE) for TMU-34(-2H) to TMU-5.

A number of 10 ml screw cap glass vial was used for SALE procedure. 0.3 g activated TMU-34(-2H) added to each one of glass vials and followed by addition of 10 ml BPDH ligand solution which had been prepared by dissolvation of 1 g BPDT in 100 mL of DMF (10 g.L<sup>-1</sup> ligand solution). Sampling for monitoring the exchange process was carried out at 24 and 48 hours. Exchange procedure monitored photoluminescence spectroscopy techniques using PerkinElmer LS-55 fluorescence spectrometer.

PL experiments show that by increasing the time from 0 to 24 and then 48 hour, the emission peak of TMU-5 is enhancing (excitation wavelength: 335 nm, emission wavelength: 588 nm). This is clearly based on replacement of BPDH linker inside the pores of TMU-5. **Table S3** represents the results of linker exchange procedure.

#### Table S3. Time-dependent exchange percentage by PL method.

Time (hour)	Exchange Progress
0	0%
24	59%
48	98%

These data for exchange progress (%) are calculated by equation (2):

Exchange progress (%) = 
$$[(I_{588}^{TMU-5})]*100$$
 (2)

Where  $I_{588}$ <sup>t</sup> is maximum emission wavelength in the emission spectrum of (X%-BPDH)-TMU-34(-2H) at time t up on excitation at 335 nm and  $I_{588}$ <sup>TMU-34</sup> is maximum emission wavelength in the emission spectrum of TMU-5. Here, the name of (X%-BPDH)-TMU-34(-2H) represent the percentage (X%) of exchanged DPT linkers inside the TMU-34(-2H) framework with H<sub>2</sub>DPT linkers to synthesis frameworks with different ratios of BPDH linker to approve the effect of functional linker on the Knoevenagel condensation.

For TMU-34(-2H), (59%-BPDH)-TMU-34(-2H), (98%-BPDH)-TMU-34(-2H) and TMU-5 framework, there are 0%, 59%, 98% and 100% of BPDH pillar spacer in the framework. The results of GC analysis (**Table S4**) show that after exchange reaction, by increasing the percentage of BPDH ligand, the reaction conversion at 30 min is increased.

**Table S4.** Results of Knoevenagel condensation by TMU-34(-2H), (59%-BPDH)-TMU-34(-2H), (98%-BPDH)-TMU-34(-2H) and TMU-34 frameworks after 60 min.

TMU-Framework	Reaction conversion
ТМИ-34(-2Н),	65%
(59%-BPDH)-TMU-34(-2H)	83%
(98%-BPDH)-TMU-34(-2H)	>99 %
TMU-34	>99 %