Novel europium complexes covalently bonded to MCM-41 and SBA-15: the spatial confinement effects on photoluminescence properties

Haiping Wang, Yufei Ma, Hao Tian, Ning Tang, Weisheng Liu, Qiong Wang, Yu Tang*

Supporting Informations

Experimental details for materials and organic compounds.

Material Synthesis:

MCM-41 was synthesized according to the procedure described by Mobil Corporation scientists. 1
The template solution was prepared dissolving 4.4 g of CTAB in 108 ml of deionized water and 48 ml NH₄OH (25 wt. % solution) under magnetic stirring. The suspension was heated until the solution became homogenous. 20 ml of TEOS were introduced into the template solution and giving rise to a white slurry. The mixture was magnetically stirred for 5 h at room temperature. The resulting solution was placed in a Teflon container, sealed and aged at 373K for 48 hours. The obtained suspensions were filtered, washed with deionized water and finally dried in air at room temperature. The template phase was calcined in air at 823K for 6 h.

SBA-15 was synthesized according to the procedure described by Zhao et al. 2
The template solution was prepared dissolving 3.2 g of Pluronic® P123 in 100mL of deionized water and 12 mL of 37 wt %-HCl under magnetic stirring. When the surfactant was completely dissolved, 9.6 mL of TEOS were added to the template solution and the mixture was heated for 24 h at 313 K. The resulting solution was placed in a Teflon container, sealed and aged at 373K for 48 hours. Solid silica particles were filtered, washed with deionized water and dried in air at room temperature. Finally, dried powders were calcined in air at 823K for 6 h.

Synthetic procedures for the amide-modified ordered mesoporous materials (MCM-41-NH₂ and SBA-15-NH₂). 3
A suspension of 4.0 g of 3-aminopropyltrimethoxysilane (ATPES) and 4.0 g of the calcined ordered mesoporous materials (MCM-41 or SBA-15) in 100 ml of toluene was heated to reflux with stirring. After heating for 6 h, the solution (10 ml) containing methanol and toluene was distilled out from the mixture. 10 ml of methanol–toluene solution was distilled again after an additional 6 h refluxing. The mixture was refluxed again for 12 h and cooled. The powder sample was centrifugation and washed with a mixture of toluene and menthol (1:1). The amide-functionalized mesoporous materials were dried in vacuum at 323K for 12h.

General Synthetic Procedures for the intermediates [MCM-41-(a∼f) and SBA-15-(a∼f)].
The amide-modified ordered mesoporous materials (0.6 g) was refluxed with the precursors of
the ligands (1 mmol) in 30 mL mixed solvent (V (chloroform) / V (methanol) = 7 / 3) for 18 h. The resulting solid was centrifugation, washed repeatedly with chloroform and finally dried in vacuum at 323K for 12h.

**General Synthetic Procedures for the mesoporous hybrid materials [MCM-41-(a ~ f)-Eu(NO3)3 and SBA-15-(a ~ f)-Eu(NO3)3].**

The intermediates [MCM-41-(a ~ f) and SBA-15-(a ~ f)] (0.2g) was refluxed with Eu(NO3)3·6H2O (0.05 mmol) in acetonitrile for 18 h. The resulting solid was centrifugation, washed repeatedly with acetonitrile and finally dried in vacuum at 323K for 12h.

**Organic Compounds Synthesis:**

**General Synthetic Procedures for 1a-1f.**

A mixture of (3.2g, 20mmol), (20mmol), K2CO3 (3.31g, 2.4mmol), and KI (1.5g, 10mmol) in DMF (30 mL) was stirred at 80°C for 12h. After cooling, the mixture was poured into 300mL of ice water and allowed to stand overnight. The deposited brown solid was extracted with CHCl3 (3×40mL) and the solvent was removed in vacuo. The dark brown compound was purified by flash chromatography (silica gel) using the mixed solution of petroleum ether and ethyl acetate (4:1) as eluent.

**2-(2-methylquinolin-8-yloxy)-N-benzylacetamide (1a)**

![Structure of 2-(2-methylquinolin-8-yloxy)-N-benzylacetamide (1a)](image)

1H NMR (400MHz, CDCl3, ppm): δ 8.952 (s, 1H), 8.035-8.015 (d, 1H, J = 8.0 Hz), 7.501-7.476 (dd, 1H, J = 8.0 Hz, J = 2.0 Hz), 7.456-7.407 (m, 1H), 7.255-7.179 (m, 7H), 4.887 (s, 2H), 4.541-4.527 (d, 2H, J = 5.6 Hz), 2.461 (s, 3H). Mass (EI): m/z 307 (M+1), 248 (0.01), 172 (1.0), 91 (0.34), 77(0.19), 65 (0.15).

**2-(2-methylquinolin-8-yloxy)-N-phenylacetamide (1b)**

![Structure of 2-(2-methylquinolin-8-yloxy)-N-phenylacetamide (1b)](image)

1H NMR (400MHz, CDCl3, ppm): δ 10.192 (s, 1H), 8.055-8.034 (d, 1H, J = 8.0 Hz), 7.493-7.470 (dd, 1H, J = 8 Hz, J = 1.2 Hz), 7.438-7.399 (t, 1H, J = 8 Hz), 7.342-7.302 (t, 3H, J = 8 Hz), 7.243-7.221 (dd, 1H, J = 7.6 Hz, J = 1.2 Hz), 7.130-7.093 (t, 1H, J = 7.6 Hz), 4.905 (s, 2H), 2.789 (s, 3H). Mass (EI): m/z 292 (M+), 200(0.15), 172(1.0), 144(0.40), 115(0.31), 77(0.32), 65(0.30).

**2-(2-methylquinolin-8-yloxy)-N,N-diphenylacetamide (1c)**

![Structure of 2-(2-methylquinolin-8-yloxy)-N,N-diphenylacetamide (1c)](image)
$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 7.997-7.976 (d, 1H, $J = 8.4$ Hz), 7.375-7.261 (m, 10H), 6.993-6.972 (dd, 1H, $J = 6.8$ Hz, $J = 1.6$ Hz), 4.910 (s, 2H), 2.754 (s, 3H). Mass (ESI): $m/z$ 369 (M$^+1$).

2-(2-methylquinolin-8-yloxy)-N,N-diisopropylacetamide (1d)

$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 7.984-7.956 (dd, 1H, $J = 8.4$ Hz, $J = 2.8$ Hz), 7.349-7.330 (dd, 2H, $J = 4.8$ Hz, $J = 2.4$ Hz), 7.278-7.250 (dd, 1H, $J = 4.8$ Hz, $J = 2.4$ Hz), 7.208-7.178 (m, 1H, $J = 5.2$ Hz), 4.969-4.954 (m, 2H), 4.452-4.442 (m, 1H), 3.372-3.361 (m, 1H), 2.766-2.741 (m, 3H), 1.368 (s, 6H), 1.131 (s, 6H). Mass (EI): $m/z$ 301 (M$^+1$), 200 (0.10), 172 (1.00), 43 (1.00).

2-(2-methylquinolin-8-yloxy)-1-(piperidin-1-yl)ethanone (1e)

$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 8.002-7.981 (d, 1H, $J = 8.4$ Hz); 7.382-7.330 (m, 2H), 7.297-7.275 (d, 1H, $J = 8.8$ Hz), 7.174-7.151 (dd, 1H, $J = 6.4$ Hz, $J = 2.8$ Hz), 5.024 (s, 2H), 3.684-3.659 (t, 2H, $J = 5.2$ Hz), 3.557-3.532 (t, 2H, $J = 5.2$ Hz), 2.761 (s, 3H), 1.583-1.498 (m, 6H). Mass (EI): $m/z$ 285 (M$^+1$), 200 (0.03), 172 (1.00), 41 (0.37).

2-(2-methylquinolin-8-yloxy)-1-morpholinoethanone (1f)

$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 8.024-8.003 (d, 1H, $J = 8.4$ Hz), 7.419-7.370 (m, 2H), 7.317-7.299 (d, 1H, $J = 8.4$ Hz), 7.180-7.158 (dd, 1H, $J = 7.2$ Hz, $J = 1.6$ Hz), 5.026 (s, 2H), 3.857-3.835 (t, 2H, $J = 4.4$ Hz), 3.613-3.589 (s, 6H), 2.754 (s, 3H). Mass (EI): $m/z$ 286 (M$^+$), 200 (0.02), 172 (1.00), 159 (0.26), 143 (0.18), 115 (0.16), 56 (0.19), 42 (0.17).

**General Synthetic Procedures for the precursors of the ligands (2a-2f).**

A solution of 1a-1f (10mmol) in dioxane (20mL) was heated to 80 °C. To the solution was added SeO$_2$ in several portions and the mixture stirred at 80 °C for 8h. The mixture was filtered to remove Se and washed with dioxane (5mL). The solution was concentrated to give a yellow crude product and the pure product was obtained by flash chromatography (silica gel) using ethyl acetate as eluent.

2-(2-formylquinolin-8-yloxy)-N-benzylacetamide (2a)

1H NMR (400MHz, CDCl₃, ppm): $\delta$ 7.997-7.976 (d, 1H, $J = 8.4$ Hz), 7.375-7.261 (m, 10H), 6.993-6.972 (dd, 1H, $J = 6.8$ Hz, $J = 1.6$ Hz), 4.910 (s, 2H), 2.754 (s, 3H). Mass (ESI): $m/z$ 369 (M$^+1$).
$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 9.700-9.698 (d, 1H, $J = 0.8$ Hz), 8.305-8.284 (d, 1H, $J = 8.4$ Hz), 8.183 (s, 1H), 8.011-7.990 (d, 1H, $J = 8.4$ Hz), 7.666-7.626 (t, 1H, $J = 8.4$ Hz), 7.596-7.572 (dd, 1H, $J = 8.4$ Hz, $J = 1.2$ Hz), 7.294-7.231 (m, 6H), 4.905 (s, 2H), 4.562-4.548 (d, 2H, $J = 5.6$ Hz). Mass (EI): $m/z$ 320 (M⁺), 291 (0.03), 215 (0.05), 186 (1.00), 106 (0.40), 91 (0.82), 77 (0.29), 65 (0.29).

2-(2-formylquinolin-8-yloxy)-N-phenylacetamide (2b)

$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 10.305 (s, 1H), 9.495 (s, 1H), 8.370-8.349 (d, 1H, $J = 8.4$ Hz), 8.130-8.110 (d, 1H, $J = 8.4$ Hz), 7.698-7.615 (m, 4H), 7.390-7.350 (t, 2H, $J = 8$ Hz), 7.315-7.293 (dd, 1H, $J = 0.4$ Hz, $J = 0.4$ Hz), 7.181-7.144 (t, 1H, $J = 0.4$ Hz), 4.949 (s, 2H). Mass (EI): $m/z$ 306 (M⁺), 214 (0.02), 186 (1.00), 77 (0.18), 65 (0.18).

2-(2-formylquinolin-8-yloxy)-N,N-diphenylacetamide (2c)

$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 10.251 (s, 1H), 8.278-8.257 (d, 1H, $J = 8.4$ Hz), 8.053-8.032 (d, 1H, $J = 8.4$ Hz), 7.608-7.568 (t, 1H, $J = 8$ Hz), 7.508-7.485 (d, 2H, $J = 8.4$ Hz), 7.330 (m, 9H), 7.152-7.133 (d, 1H, $J = 8$ Hz), 5.018 (s, 2H). Mass (EI): $m/z$ 382 (M⁺), 263 (0.0046), 234 (0.0015), 186 (1.00), 167 (0.33), 77 (0.31).

2-(2-formylquinolin-8-yloxy)-N,N-diisopropylacetamide (2d)

$^1$H NMR (400MHz, CDCl₃, ppm): $\delta$ 10.288-10.287 (d, 1H, $J = 0.4$ Hz), 8.294-8.273 (d, 1H, $J = 8.4$ Hz), 8.072-8.051 (d, 1H, $J = 8.4$ Hz), 7.614-7.573 (t, 1H, $J = 8.4$ Hz), 7.505-7.485 (d, 1H, $J = 8$ Hz), 7.289-7.273 (d, 1H, $J = 6.4$ Hz), 5.025 (s, 2H), 4.382-4.316 (m, 1H), 3.469-3.403 (m, 1H), 1.412-1.395 (d, 6H, $J = 6.8$ Hz), 1.216-1.200 (d, 6H, $J = 6.4$ Hz). Mass (EI): $m/z$ 315 (M⁺+1), 214 (0.10), 186 (1.00), 86 (0.40), 43 (1.00).
8-(2-oxo-2-(piperidin-1-yl)ethoxy)quinoline-2-carbaldehyde (2e)

\[
\begin{align*}
\text{1H NMR (400MHz, CDCl3, ppm): } & \delta 10.280-10.278 \text{ (d, } 1H, J = 0.8 \text{ Hz}), 8.300-8.279 \text{ (d, } 1H, J = 8.4 \text{ Hz}), 8.078-8.057 \text{ (d, } 2H, J = 8.4 \text{ Hz}), 7.619-7.579 \text{ (t, } 1H, J = 8 \text{ Hz}), 7.521-7.498 \text{ (dd, } 1H, J = 8 \text{ Hz, } J = 0.8 \text{ Hz}), 7.283-7.261 \text{ (dd, } 1H, J = 7.6 \text{ Hz, } J = 1.2 \text{ Hz}), 5.090 \text{ (s, } 2H), 3.675-3.649 \text{ (t, } 2H, J = 5.6 \text{ Hz}), 3.588-3.561 \text{ (t, } 2H, J = 5.6 \text{ Hz)}, 1.645-1.533 \text{ (m, } 6H). \\
\text{Mass (EI): } & m/z \text{ 298 (M\textsuperscript+), 299 (M\textsuperscript++1), 215 (0.05), 186 (1.00), 97 (0.48), 84 (0.82), 41(0.99).}
\end{align*}
\]

8-(2-morpholino-2-oxoethoxy)quinoline-2-carbaldehyde (2f)

\[
\begin{align*}
\text{1H NMR (400MHz, CDCl3, ppm): } & \delta 10.261-10.260 \text{ (d, } 1H, J = 0.4 \text{ Hz}), 8.321-8.300 \text{ (d, } 1H, J = 8.4 \text{ Hz}), 8.089-8.068 \text{ (d, } 1H, J = 8.4 \text{ Hz}), 7.635-7.595 \text{ (t, } 1H, J = 8 \text{ Hz}), 7.552-7.529 \text{ (dd, } 1H, J = 8.4 \text{ Hz, } J = 0.8 \text{ Hz}), 7.284-7.263 \text{ (dd, } 1H, J = 7.6 \text{ Hz, } J = 0.8 \text{ Hz}), 5.103 \text{ (s, } 2H), 3.820-3.7965 \text{ (t, } 2H, J = 4.4 \text{ Hz}), 3.685-3.656 \text{ (m, } 6H). \\
\text{Mass (EI): } & m/z \text{ 300 (M), 271 (0.02), 215 (0.04), 202 (0.05), 186 (1.00), 127 (0.26), 56 (0.41), 42 (0.30).}
\end{align*}
\]
### Table S1 Elemental analysis of mesoporous hybrid materials

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<th>H (%)</th>
<th>N (%)</th>
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Fig. S1 FT-IR spectra of MCM-41 type hybrid materials.
Fig. S2 FT-IR spectra of SBA-15 type hybrid materials.
Fig. S3 TEM images of M41c-Eu (a) and S15c-Eu (b).
Fig. S4 N₂ adsorption/desorption isotherms of the mesoporous hybrid materials.

References
Copies of NMR spectra of organic compounds.

2-(2-methylquinolin-8-yloxy)-N-phenylacetamide (1a)

2-(2-methylquinolin-8-yloxy)-N-benzylacetamide (1b)
2-(2-methylquinolin-8-yloxy)-N,N-diphenylacetamide (1c)

2-(2-methylquinolin-8-yloxy)-N,N-diisopropylacetamide (1d)
2-(2-methylquinolin-8-yloxy)-1-(piperidin-1-yl)ethanone (1e)

2-(2-methylquinolin-8-yloxy)-1-morpholinoethanone (1f)
(2a) 2-(2-formylquinolin-8-yloxy)-N-phenylacetamide

2-(2-formylquinolin-8-yloxy)-N-benzylacetamide (2b)
2-(2-formylquinolin-8-yloxy)-N,N-diphenylacetamide (2c)

2-(2-formylquinolin-8-yloxy)-N,N-diisopropylacetamide (2d)
8-(2-oxo-2-(piperidin-1-yl)ethoxy)quinoline-2-carbaldehyde (2e)

8-(2-morpholino-2-oxoethoxy)quinoline-2-carbaldehyde (2f)