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Highly switchable and shape-controlled photocatalysis within dye-based metal-organic frameworks

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Photocatalysis could promote challenging chemical reactions via green energy, however, controlling the chemo-/stereoselectivity of photocatalysis has long been hindered due to the dearth of effective binding strategy for substrates and the in situ generated radical species. Imposing additional interactions on substrates or radical species is beneficial to orienting the conformation of substrates or intermediates, favouring the chemo- or stereocontrol of photocatalysis especially when there are no covalent binding sites on the substrates. The other strategy is to "fix" the reactive radical species via inner sphere modes of complexation with transition metal ions. By merging photoactive organic dyes and transition metals within metal-organic frameworks, the synergy of photocatalytic and transition metal catalytic cycles would be carried out, and the abundant non-covalent interactions sites within MOF channels are capable of imposing conformational orientation on substrates, resulting in perfect stereocontrol. When the MOF photocatalyst is comprised of Zn_4O nodes and triarylamine-based ligand, aryltrifluoromethylation of unsaturated olefins could be conducted with enhanced diastereoselectivity. While the combination of $Cu_2(O_2CR)_4$ paddle-wheel nodes and triarylamine-based ligand within MOFs switches to suppress the radical cyclization process, favouring the atom transfer radical addition (ATRA). The non-covalent interaction induced shape-control has been confirmed by X-ray single crystal diffraction experiments on the MOFs crystals encapsulating substrates. And the asymmetrically catalyzed ATRA is primarily examined after introducing chiral auxiliaries into the MOFs.

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Diagnostic value of tumor markers in lung adenocarcinoma-associated cytologically negative pleural effusions

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Cytology fails to detect neoplastic cells in 40–50% of malignant pleural effusions (PEs), which commonly accompany lung adenocarcinomas. Diagnostic accuracy of various tumor markers in lung adenocarcinoma-associated cytologically negative pleural effusions (LAC-CNPEs) has been poor. This study aimed to maximize diagnostic efforts in distinguishing LAC-CNPEs from benign PEs. Pleural effusion samples were collected from 74 lung adenocarcinoma patients with associated cytologically positive (41) and negative (33) effusions, and from 99 patients with benign conditions including tuberculosis (26), pneumonia (28), congestive heart failure (25), and liver cirrhosis (20). We evaluated the diagnostic sensitivity and optimal cutoff points for tumor markers Her-2/neu, Cyfra 21-1, and carcinoembryonic antigen (CEA) to distinguish LAC-CNPEs from benign PEs. Mean levels of Her-2/neu, Cyfra 21-1, and CEA were significantly higher in LAC-CNPEs than in benign pleural effusions (P= 0.0050, =0.0039, and <0.0001, respectively). The cutoff points for Her-2/neu, Cyfra 21-1, and CEA were optimally set at 3.6 ng/mL, 60 ng/mL, and 6.0 ng/mL. Their sensitivities ranged from 12.1%, to 30.3%, to 63.6%, respectively. CEA combined with Cyfra 21-1 increased diagnostic sensitivity to 66.7%. False-positive rates of these markers in benign PEs were 6.1%, 2.0% and 0%, respectively. Combining CEA with Cyfra 21-1 will provide the best differentiation between LAC-CNPEs and benign PEs with two tumor markers to date, and allows early diagnosis and early treatment for two-thirds of affected patients.

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