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Review

Luminescent sensors based on metal-organic frameworks

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ABSTRACT

Metal-organic frameworks (MOFs) are a fascinating class of highly porous materials composed of metal ions/clusters and organic linkers, which promise great potential in numerous fields. Recently, the use of MOFs as luminescent sensors has been extensively explored due to their unique crystallinity, tunable porosity and structural diversity. In this review, we intend to highlight some of recent studies in this

Abbreviations: MOFs, metalorganic frameworks; PL, photoluminescence; PCPs, porous coordination polymers; LMCT, ligand-to-metal charge transfer; MLCT, metal-to-ligand charge transfer; LUMO, lowest unoccupied molecular orbital; CB, conduction band; SBUs, secondary building units; LMOFs, luminescent metalorganic frameworks; GC, gas chromatography; pytpy, 2,4,6-tris(4-pyridyl)pyridine; EnT, ligand-to-metal energy transfer; H_3BTC, 1,3,5-benzenetricarboxylic acid; MIL, Materials of Institute Lavoisier; TPTZ, {4-[4-(1H-1,2,4-triazol-1-yl)phenyl]phenyl}-1H-1,2,4-triazole; IPA, 1,3-benzenedicarboxylic acid; H_2BPDC, 4,4′-biphenyldicarboxylic acid; H_2SDBA, 4,4′-sulfonyldibenzoic acid; H_2BETC, benzene-1,2,4,5-tetracarboxylic acid; DMF, N,N′-dimethylformamide; H_4BPTC-1, benzophenone-3,3,4,4′-tetracarboxylic acid; H_4BPTC-2, biphenyl-3,3′,5,5′-tetracarboxylic acid; NTU, Nanyang Technological University; H_2DOBDC, 2,5-dihydroxyterephthalic acid; H_3BTB, 1,3,5-benzenetribenzoic acid; Phen, 1,10-phenanthroline; $H_4BPDSDC$, biphenyl-3,3′-disulfonyl-4,4′-dicarboxylic acid; PCN, porous coordination network; TCPP, tetra(4-carboxyphenyl)porphyrin; HEPES, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; H_6TTHA, 1,3,5-triazine-2,4,6-triamine hexaacetic acid; UiO, Universitetet i Oslo; H_2ABDC, 2-amino benzene-1,4-dicarboxylic acid; $H_2PhenDCA$, 1,10-phenanthroline-2,9-dicarboxylic acid; 55′-H2BPYDC, 2,2′-bipyridine-5,5′-dicarboxylic acid; TTA, 2-thenoyltrifluoroacetone; NMOFs, nanoscale metalorganic frameworks; FITC, fluorescein isothiocyanate; PBS, phosphate-buffer saline; VOCs, volatile organic compounds; AIE, aggregation-induced emission; RIR, restriction of intramolecular rotation; TPE, tetraphenylethene; NUS, National University of Singapore; H_2DPEB, 4,4′-(2,2-diphenylethene-1,1-diyl)dibenzoic acid; THF, tetrahydrofuran; H_2FDA, furan-2,5-dicarboxylic acid; CPM, crystalline porous materials; BEnT, energy back transfer; Hppy, 2-phenylpyridine; DBP-Pt, Pt-5,15-di(p-benzoato) porphyrin; H_2QPDC-NH_2, amino-quaterphenyldicarboxylaic acid; RITC, Rhodamine-B isothiocyanate; MAF, metal azolate framework; TMBPZ, 3,3′,5,5′-tetramethyl-4,4′-bipyrazole; TPC4A, 2,8,14,20-tetraphenyl-6,12,18,24-tetra-methoxy-4,10,16,22-tetra-carboxy-methoxy-resorcin[4]arene; TNC4A, 2,8,14,20-tetra-1-naphthal-6,12,18,24-tetra-methoxy-4,10,16,22-tetra-carboxy-methoxy resorcin[4]arene; TNP, 2,4,6-trinitrophenol; TABD-COOH, (4,4′-((Z,Z)-1,4-diphenylbuta-1,3-diene-1,4- diyl)dibenzoic acid; NTO, 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one; TPPE, 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethane; AFB_1, Aflatoxins B_1; BUT, Beijing University of Technology; H_3CTTA, 5′-(4-carboxyphenyl)-2′,4′,6′-trimethyl-[1,1′:3′,1″-terphenyl]-4,4″-dicarboxylic acid; H_3TTNA, 6,6′,6″- (2,4,6-trimethylbenzene-1,3,5-triyl)tris(2-naphthoic acid); NZF, nitrofurazone; NFT, nitrofurantoin; ssDNA, single-stranded DNA; 5-FAM, 5-carboxyfluorescein; tDNA, target DNA; H_2DMBDC, 2,5-dimethoxy-1,4-benzenedicarboxylic acid; D-H_2cam, D-camphoric acid; H_3IMDC, 4,5-imidazole dicarboxylic acid; H_2BPDA, biphenyl-3,5-dicarboxylic acid; H_2BDC, benzene-1,4-dicarboxylate; ZJU, Zhejiang University; NTB, 4,4′,4″-nitrilotrisbenzoic acid; DMA, *N,N*′-dimethylacetamide; NB, nitrobenzene; BPPA, bis(4-(pyridine-4-yl)phenyl)amine); H_2ABA, 4,4′-azanediyldibenzoic acid; H_2oba, 4,4′-oxybis(benzoic acid)); NP, 4-nitrophenol; PA, picric acid; 2, 6-H_2NDC, 2,6-naphthalenedicarboxylic acid; PCA, 4-pyridinecarboxylic acid; TPT, *p*-terphenyl-3,4″,5-tricarboxylic acid; 1, 4-H_2NDC, 1,4-naphthalenedicarboxylic acid; DIA, 9,10-bis(1*H*-imidazol-1-yl)anthracene; DEF, *N,N*′-diethylformamide; H_3CPEIP, 5-((4-carboxyphenyl)ethynyl)isophthalic acid; H_4ETTC, 4′,4‴,4⁗′,4‴‴′-(ethene-1,1,2,2-tetrayl)tetrakis(1,1′-biphenyl-4-carboxylic acid); Ur, urotropine; TNT, trinitrotoluene; DNB, dinitrobenzene; DNT, dinitrotoluene; BPEE, 1,2-bipyridylethene; DMNB, 2,3-dimethyl-2,3-dinitrobutane; H_4TPTC, terphenyl-3,3″,5,5″-tetracarboxylic acid; apy, aminopyridine; bpy, 4,4′-bipyridine; 4-NBA, 4-nitrobenzoic acid; 4-BPDH, 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene; NT, 4-nitrotoluene; DPYB, 1,4-di(pyridin4-yl)benzene; DIBP, 4,4′-di(1H-imidazol-1-yl)-1,1′-biphenyl; HFIPBB, 4,4′-(hexafluoroisopropylidene)bis(benzoic acid); bpe, *trans*-1,2-bis(4-pyridyl)ethylene; BPNO, 4,4′-dipyridyl-N,N′-dioxide; NM, nitromethane; NE, nitroethane; H_2ADDA, 3,3′-(anthracene-9,10-diyl)diacrylic acid; DUT, Dresden University of Technology; H_2CPMA, bis(4-carboxyphenyl)-*N*-methylamine; 4, 4′-H_2DCBPY, 2,2′-bipyridine-4,4′-dicarboxylic acid; H_3TTCA, triphenylene-2,6,10-tricarboxylic acid; 3-Hqlc, quinoline-3-carboxylic acid; H_2ox, oxalic acid; H_2MFDA, 9,9-dimethylfluorene-2,7-dicarboxylic acid; H_2PZDC, 3-(1H-pyrazol-3-yl) benzoic acid; NMP, *N*-methyl-2-pyrrolidone; DBM, 1,3-diphenylpropane-1,3-dione; bpy, 2,2′-dipyridine; H_2PYDC, 2,6-pyridinedicarboxylic acid; H_4ODA, 2,2′,3,3′-oxidiphthalic acid; H_3TCA, 4,4′,4″-tricarboxytriphenylamine; H4QPTCA, [11′:4′,1″:4″,1‴-quaterphenyl]-3,3‴,5,5‴-tetracarboxylic acid; H_3TATAB, 4,4′,4″-*s*-triazine-1,3,5-triyltri-*p*-aminobenzoic acid; H_3TPT, *p*-terphenyl-3,4″,5-tricarboxylic acid; H_4ABTC, 11′-azobenzene-3,3′,5,5′-tetracarboxylic acid; HMTA, hexamethylenetetramine; **L^1^**, 4,4′-(9,9-dibutyl-9H-fluorene-2,7-diyl)dipyridine; **L^2^**, 4,4′-dicarboxylate-2,2′-dipyridine; **L^3^**, 4,4′-(2,5-bis-(methylthio)-1,4-phenylene)dipyridine; **L^4^**, *p*-terphenyl-3,4″,5-tricarboxylic acid; **L^5^**, 2-(pyrene-1-imine)terephthalic acid; **L^6^**, (E)-4-(2-carboxyvinyl) benzoic acid; **L^7^**, 1-benzimidazolyl-3,5-bis(4-pyridyl)benzene); **L^8^**, 2,6-bis((3,5-dimethyl-1H-pyrazol-4-yl)methyl)pyridine; **L^9^**, 2′,5′-bis(methoxymethyl)-[1,1′:4′,1″-terphenyl]-4,4″-dicarboxylate; **L^10^**, 5-hydroxy-1,2,4-benzenetricarboxylic acid; **L^11^**, 4-(1*H*-tetrazol-5-yl)-*N*-[4-(1*H*-tetrazol-5-yl)phenyl]benzamide; **L^12^**, 2′-amino-[1,1′:4′,1″terphenyl]-4,4″-dicarboxylate; **L^13^**, 2-phenylpyridine-5,4′-dicarboxylic acid; **L^14^**, bis-(3,5dicarboxy-phenyl)terephthalamide; **L^15^**, 9*H*-Carbazole-3,6-dicarboxylic acid; **L^16^**, 2,5-(6-(4-carboxyphenylamino)-1,3,5-triazine-2,4-diyldiimino)diterephthalic acid; **L^17^**, 3,3′-(thiophene-2,5-diyl)dibenzoic acid; **L^18^**, $Ir(ppy)_2$(dcbpy); **L^19^**, 4,4′,4″-s-triazine-1,3,5-triyltri-*m*-aminobenzoate; **L^20^**, 1,4-bis(5-carboxy-1H-benzimidazole-2-yl)benzene; **L^21^**, 4′-(3,5-dicarboxyphenyl)-4,2′:6′,4″-terpyridine; **L^22^**, 4,4′-(pyridine-3,5-diyl)diisophthalic acid; **L^23^**, 4-(((1 H-imidazol-2-yl)methylene)amino)benzoic acid.

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active research area and update the database of various luminescent MOF-based sensors on the basis of different sensing targets including ions, organic molecules, and gases, and temperature.

Contents

1. Introduction

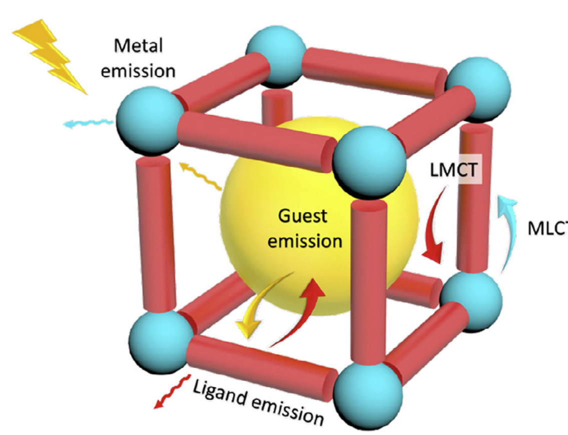
Luminescent materials have long held a strong fascination for scientists and lay people alike. They are those materials that release energy in terms of, other than thermal radiation, light upon excitation by outside stimulus, such as X-rays, electron beams, UV light, or even mechanical phenomenon [1,2]. The key to spark luminescence of the materials, hence, is to block non-radiative pathways, and this is often involved with building rigid scaffolding and preventing molecular vibrations through material architecture [3]. Recently, luminescent materials have gained much attention for their use as chemical sensing agents or in the realm of biomedical science [4]. The main advantage of luminescent materials over other transduction ones is that they can quickly and easily give a colorimetric response to stimuli. Additionally, luminescent materials can be used in conjunction with spectrophotometers, allowing the identification of the sensed material based on the characteristic absorption and emission shifts [5].

As a viable luminescent sensor, several requirements need to be satisfied. First, the material needs to respond to an analyte in a given area. The capability of trapping analyte molecules to a desired local concentration would contribute to high sensitivity. Secondly, an excellent sensor should be insensitive towards possible undesired luminescent quenching, which could be induced by testing environments. Moreover, chemical and physical stability are also required so that efficient testing can be performed in extreme environments.

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are an emerging class of crystalline porous materials, which have received considerable attention in the past decades [6]. They have been proven successful in many applications, including gas storage [7] and separation [8], heterogeneous catalysis [9], light harvesting and chemical sensing [6,10], as well as drug delivery and bioimaging [11]. Among numerous reported luminescent materials, luminescent MOFs (LMOFs) have recently bloomed out as potential chemical sensors due to their easily induced luminescence, diverse advantages in structural and functional components, and various detecting mechanisms.

1.1. Origins of luminescence

With the inherent hybrid nature, luminescence of MOFs can arise from either organic linkers or metal ions (Scheme 1). Linker-centered luminescence is the most common type, which includes three subtypes: linker emission, ligand-to-metal charge transfer (LMTC) and metal-to-ligand charge transfer (MLCT). Fluorescent linkers generally contain aromatic or π-conjugated backbones in many reported LMOFs, which give linker emission upon irradiation [12]. MLCT can be seen in MOFs composed of



Scheme 1. Representation of possible emission modes in MOFs. Inorganic SBUs, blue spheres; Organic linkers, red cylinders; Guest chromophores, yellow sphere inside.

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