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Achieving exceptionally high luminescence quantum efficiency by immobilizing an AIE molecular chromophore into a metal-organic framework

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We design a new yellow phosphor with high quantum yield by immobilizing a preselected chromophore into a rigid framework. Coating a blue light-emitting diode (LED) with this compound readily generates white light with high luminous efficacy. The new yellow phosphor demonstrates great potential for use in phosphor-converted white LEDs.

Light-emitting diodes (LEDs), one of the main branches of solid-state lighting (SSL) technology, have rapidly emerged in various lighting applications, owing to their higher efficiency, longer lifetime, and lower energy consumption relative to incandescent and fluorescent bulbs. White light-emitting diodes (WLEDs) are of particular importance because of the high demand for general illumination and displays. The energy impact of LEDs is profound: The U.S. Environmental Protection Agency (EPA) estimates that the nation can save nearly $700 million per year on energy cost, if every household substitutes just one incandescent lamp with an ENERGY STAR rated LED.[1] The U.S. Department of Energy also acknowledges SSL as a significant climate change solution as this technology could cut the nation's lighting energy consumption by almost one half.[2] In one of the largest retrofitting projects in the US, New York City plans to replace all of its 250,000 street lights with LEDs, aiming at a 30% drop of greenhouse gas emission by 2017.[3] One way to construct WLEDs is by the combination of three single-chip diodes, namely red, green, and blue (RGB) LEDs. A drawback of this multi-chip system is its high cost. Another method is coating phosphors on single-chip LEDs, which are also known as phosphor-converted WLEDs (PC-WLEDs). For example, either a mixture of RGB (or other multicomponent) phosphors or a white phosphor which emits throughout the visible region can be coated on UV LEDs.[4] Similarly, yellow phosphors can be excited by blue LEDs to produce white light, such as the commercially available YAG:Ce^{3+} coupled with blue LEDs.[5] Considering the wide availability and low cost of blue LEDs, yellow phosphor based PC-WLEDs are preferred.[6] The vast majority of currently available yellow phosphors rely heavily on the rare-earth elements.[7] However, due to the increasing demand of these elements in many other high-tech applications, their prices have increased by 4 to 49 times from 2001 to 2011. For example, the prices of Y, Eu, and Tb, the three essential ingredients of phosphors used in general lighting technologies have increased by 400%, 600%, and 1600% respectively.[8] The search for rare-earth-free yellow phosphors is becoming increasingly urgent.[8]
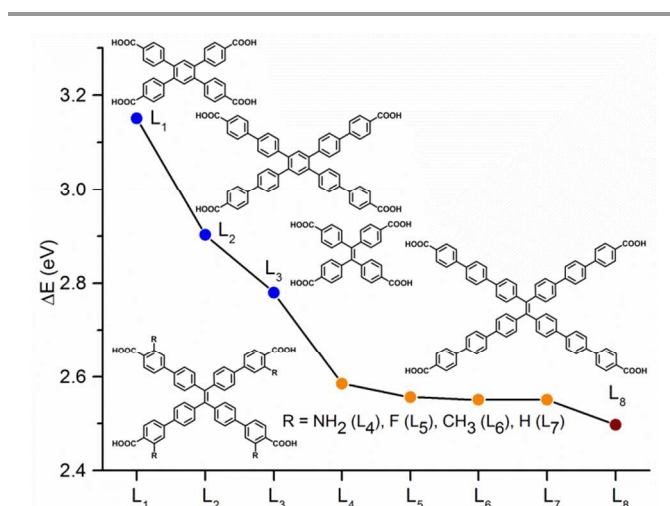
Figure 1. Estimated HOMO-LUMO energy gaps of ligands at B3LYP/DGDZVP.[9] ΔE is normalized to the experimental value of L_7 (or H_4tcbpe) extrapolated from the diffuse reflectance spectrum. Full ligand names are in the ESI.

Molecular aggregation often plays a key role in the photoluminescence (PL) properties of a phosphor. Upon aggregation, the PL of a phosphor may be subject to aggregation-caused quenching (ACQ) and/or aggregation-induced emission (AIE).[10] Phosphors with AIE characteristics are generally more appealing. In designing highly efficient yellow-emitting phosphors, our strategy is to preselect an AIE type ligand with appropriate emission energy. We began by evaluating the HOMO-LUMO energy gap (ΔE) of a series of conjugated organic ligands with a focus on chromophores containing the tetraphenylethylene (tpe) core, which is a typical AIE moiety.[10a, 11] As shown in Figure 1, varying the conjugation of organic chromophores can systematically tune ΔE. For example, H_4tcpe (tetrakis(4-carboxyphenyl)ethylene) (L_3) is a reasonable starting point since its internal quantum yield (IQY) is as high as 47 %.[12] However, its emission is too close to blue (λ_{em} = 480 nm).[13] To red-shift the emission peak, we decrease ΔE by increasing the arm length extended from the tpe core (e.g. L_4 to L_8 in Figure 1). Thus we synthesized the targeted ligand H_4tcbpe (L_7), 4',4''',4''''',4'''''''-(ethene-1,1,2,2-

tetrayl)tetrakis ([1,1'-biphenyl]-4-carboxylic acid) which emits near 540 nm.[14]
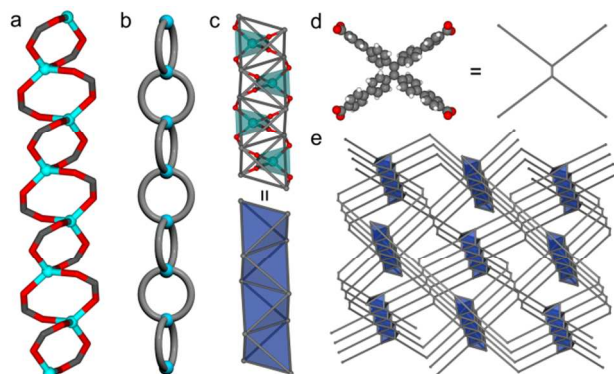
Figure 2. **a**. A chain formed along the c axis containing alternating eight-membered rings. **b**. An illustration of the chain emphasizing the alternating rings. **c**. The polyhedral representation of the SBU as an infinite rod of edge-sharing tetrahedra. **d**. The tcbpe ligand simplified as a butterfly shape. **e**. The overall simplified structure of **1** showing 1D rod SBU and 1D open channel along the c axis. Color code: H (white in **d**, omitted for clarity in **a** and **c**), C (grey), O (red), Zn (aqua).

Metal-organic frameworks (MOFs) have been extensively studied for various potential applications.[15] The strong luminescence of a number of MOFs, and especially their ability in immobilizing molecular chromophores, have further facilitated their possible use as phosphors.[16] As potential phosphors, luminescent MOFs (LMOFs) have several intrinsic advantages: The diverse building components available for the construction of LMOFs offer various sources of fluorescence, which makes it possible to design phosphors independent of rare-earth elements or elements with adverse environmental impacts (such as cadmium and selenium) — the former are the essential ingredients in current commercially available inorganic phosphors, and the latter are the key components in quantum-dot based phosphors.[17] The synthesis conditions for LMOFs are much milder than those for solid-state inorganic phosphors; the fabrication process only requires moderate heating or even no heating (e.g. reactions at room temperature), which conserves energy from the very beginning of their life cycle. Anchoring organic chromophores, especially the AIE-type, into the rigid MOF backbone effectively inhibits non-radiative decay involving ligand rotation, vibration, and torsion, potentially enhancing the overall fluorescence of the resulting compounds.[13] Our recent studies on Zn-based LMOFs have revealed that PL emissions in these structures are primarily ligand based or involve ligand-to-ligand charge transfer (LLCT), depending on the number and nature of the chosen ligands.[18] Here, we assemble an LMOF using zinc (II) as nodes and the highly luminescent near-yellow emitting chromophore, H_4tcbpe, as linker. Upon blue excitation, the resulting LMOF compound shows ligand-based yellow emission with exceptionally high quantum yield.

[Zn_2(tcbpe)·xDMA (**1**), DMA = N, N-dimethylacetamide] or LMOF-231 was synthesized solvothermally (120 $^{\circ}$C, 48 hours). It crystallizes in the monoclinic crystal system with space group $C\ 2/c$.[19] Each Zn (II) tetrahedrally coordinates to O atoms from four different tcbpe ligands. All of the carboxylate groups are bidentate with each O atom connecting a different Zn (II). Two Zn, two C, and four O atoms form an eight-membered ring in a chair-boat confirmation, which differs from the boat-boat confirmation of the rings in Zn(tbip) (H_2tbip = 5-(*tert*-butyl)isophthalic acid).[20] The rings alternate along the c axis to form a 1D chain (Figure 2a-c) that can be regarded as an infinite SBU. This type of rod-shaped SBU effectively prevents framework interpenetration.[21] Each tcbpe ligand bridges four adjacent chains (rods) to afford the three-dimensional (3D) framework with 1D channel along the c axis, as shown in Figure 2. The overall structure is a new (3,6)-c net with Point symbol $\{3^6.4^4.8^4.9\}_2\{8^3\}$ (obtained from

TOPOS).[22] The framework is porous with a BET surface area of 833 m^2/g (Figure S10). Compound **1** is thermally stable to 460 °C, making it more robust than H_4tcbpe which decomposes around 350 °C, as indicated by the thermal-gravimatric analysis (Figure S9).
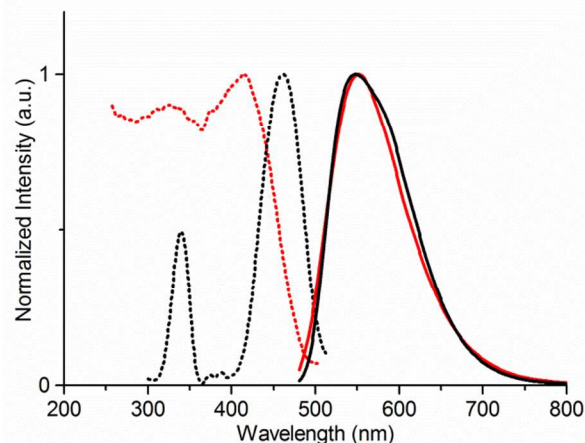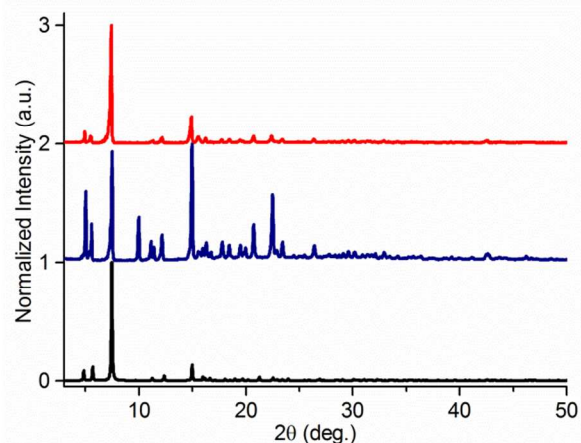
Figure 3. Top: PXRD patterns of **1'** (red), **1** (navy), and simulated pattern from single crystal analysis. Bottom: Excitation (dotted line) and emission (solid line) spectra of **1'** (red) and YAG:Ce^{3+} (black).

Room temperature optical absorption, emission, and quantum yield measurements were performed on both as-made and outgassed samples of LMOF-231 in air. With a 2.55 eV optical band gap, LMOF-231 (**1**) exhibits ligand based emission in the near-yellow region. The evacuation of **1** gives rise to the guest-free LMOF-231' (or **1'**) with a lower band gap of 2.30 eV (Figure S11). Susceptible to a wide range of excitation energy, the emission of **1'** falls right into the yellow region (Figure 3). The immobilization of the H_4tcbpe ligand into a rigid framework has two advantages: The rotation and torsion of phenyl rings are further inhibited, leading to increased quantum yield (Table 1).[23] The emission peak is red shifted to 550 nm in the guest-free sample producing a more yellow color (Figure S11). The IQYs of the as-made and outgassed LMOF-231 measured at blue excitation (λ_{ex} = 420 nm) are 82.5% and 95.1%, respectively (Table 1), which rival that of the commercial available phosphor YAG:Ce^{3+} (IQY = ~95%) and are the highest among all rare-earth-free blue-excitable yellow phosphors reported to date. In addition, high external quantum yield (EQY) values are obtained (Table 1). For outgassed sample, the value is as high as 96.5% of its internal QY when excited at 400 nm. This result indicates that the material is a very efficient light absorber (close to 100% absorption). The Commission International de l'Eclairage (CIE)

coordinates (Figure S15) of **1'** are (0.42, 0.54), nearly identical to those of YAG:Ce^{3+} (0.43, 0.54). The similarity of their emission properties makes **1'** a great candidate as a YAG:Ce^{3+} substitute.

Table 1. Photophysical properties of H$_4$tcbpe and compound 1.

a. Internal Quantum Yield (%)

Sample	$\lambda_{ex} = 420$ nm	$\lambda_{ex} = 440$ nm	$\lambda_{ex} = 455$ nm
H$_4$tcbpe	70.3±0.1	63.2±0.1	62.3±0.1
1	82.5±0.1	74.7±0.1	72.2±0.1
1'	95.1±0.2	81.3±0.1	76.4±0.2

b. External Quantum Yield (expressed as % of Internal Quantum Yield)

Sample	$\lambda_{ex} = 400$ nm	$\lambda_{ex} = 415$ nm	$\lambda_{ex} = 440$ nm	$\lambda_{ex} = 455$ nm
1	96.0	94.2	80.6	64.6
1'	96.5	96.0	93.3	88.7

H$_4$tcbpe, **1**, and **1'** emit at 540 nm, 540 nm, and 550 nm respectively when excited at 455 nm.

The emission color of **1'** is tunable by incorporating different solvents in its pores. To investigate the solvent effect, we studied the photo-physical properties of several solvent exchanged samples. The solvent free form emits closest to yellow, while all solvents selected in this study unanimously shift the emission peak to the higher energy region (Figure S11): N,N-diethylformamide (DEF) shifts the emission mostly dramatically by 20 nm; (ethyl acetate) EA has the minimal effect (within 5 nm). It is also worth mentioning that solvent incorporation decreases the IQY, possibly due to non-radiative excitation relaxation facilitated by solvent molecules. Therefore, the activation of **1** serves two purposes: (i) driving the emission peak more towards yellow; (ii) further boosting the IQY of the LMOF (the first boost being the anchoring effect of the framework on the AIE chromophore). We are currently working to find solvents or guest molecules which can shift the emission towards lower energy or drastically change the overall emission profile, as research of this aspect is fundamentally interesting.
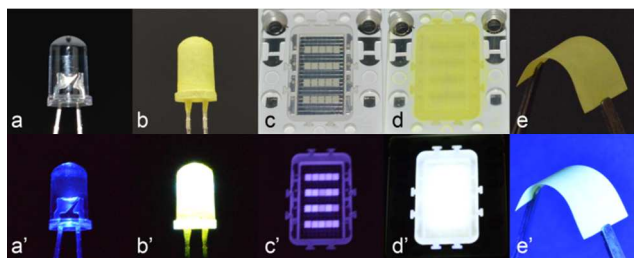
Figure 4. **a** to **d**. Blue LED bulb (455-460 nm, **a** and **b**) and plate (450-455 nm, **c** and **d**), before and after coating with solution-processed **1'** to create PC-WLEDs, with the top and bottom rows corresponding to device states 'off' and 'on', respectively. **e**. A flexible ribbon coated with **1'** under day light (**e**), and blue light (450-470 nm, LED lamp, **e'**).

To further assess the performance of **1'** as a yellow phosphor, we built PC-WLED assemblies by coating commercially available blue LEDs with a solution processed sample of **1'**. The solution processiblity of **1'** (ESI 8) allows the application of this compound to different types of surfaces, accommodating either LED bulb or plate, as shown in Figure 4. The luminous efficacy of the PC-WLED (bulb type, 455-460 nm, 5 mm chip, 20 mA, 3V) is as high as 58.9±1.5 lm/W, which is above the current thresholds for LED directional lamps (40 lm/W) and omnidirectional lamps (50 lm/W) with less than 10 W input power set by the US EPA's ENERGY STAR program.[24]

To mimic an actual LED assembly where the phosphor is encapsulated in a transparent plastic shell and test its thermal stability, we sealed the activated powder sample in Teflon (TF@**1'**). A thermal-gravimetric analysis on **1** indicates the as-made sample loses

its solvent content near 160 °C, and the structure maintains its integrity until near 460 °C. Heating TF@**1'** at different temperatures for 12 h has minimum effect on its emission, as the decrease in emission intensity is within 15% after heat treatment from 100 to 160 °C (Table S4). Thus **1',** resistant to elevated temperatures, makes a great phosphor candidate for WLEDs.

In summary, we have designed and synthesized a new AIE-type chromophore, H$_4$tcbpe. The immobilization of H$_4$tcbpe into a rigid framework structure shifts the emission of the resulting compound (LMOF-231') further into the yellow region with increased IQY and very high EQY, rivalling that of the commercially available YAG:Ce^{3+}. The thermally stable, rare-earth-free LMOF-231' can be mounted upon various type of surfaces through solution-mediated processes. With all the above merits, this material has great potential as a yellow phosphor for use in PC-WLEDs. Studies on other MOF phosphors built on high performance AIE-type ligands and their derivatives to achieve further enhanced and systematically tunable emission are currently under way.

Notes and references

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† The tcbpe ligand was synthesized by a Pd-catalysed Suzuki reaction under basic condition, followed by hydrolysis and acidification. The detailed synthesis is included in a US provisional patent filled on April 25, 2014.[14a] While we were preparing this manuscript, we noted Zhou and co-workers recently reported this ligand synthesized by a different procedure.[25]

Electronic Supplementary Information (ESI) available: LMOF-231 Synthesis and solution process, PXRD, TGA, UV-Vis and PL spectra, and computational details *etc*. CCDC 908787 and 1004908. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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