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Topology-Dependent Emissive Properties of Zirconium-Based Porphyrin MOFs

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DOI: 10.1039/x0xx00000x

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Highly ordered chromophoric linkers positioned within the metalorganic frameworks (MOFs) have the potential to mimic natural light-harvesting complexes. Herein we report topological control over the photophysical properties of MOFs via modular interchromophoric electronic coupling to manifest different steady-state singlet emissive spectra and their corresponding fluorescence lifetimes.

The light-harvesting (LH) antenna complex defines a highly efficient energy transfer machinery that near quantitatively delivers absorbed light to the reaction center.¹ Highly ordered chlorophyll and carotenoid pigments ensure sequential migration of photoinduced energy.^{1b, 2} These nanoscale architectures have motivated many scientific explorations over the past decades to design artificial antenna systems such as covalently linked polymers,³ dendrimers and various supermolecular arrays,⁴ and a wide range of self-assembled supramolecular constructs.⁵ Considering the synthetic ease and control over interchromophoric interactions, the self-assembled supramolecular approach seems to be promising as it often leads to hierarchical solid state ordering *via* noncovalent interactions.⁶

Metal-organic frameworks (MOFs), a new class of porous hybrid material,⁷ have received discernible attention in recent time for the construction of solid-state crystalline LH model system.⁸ These coordination polymers often consist of chromophoric linkers connected through inorganic nodes. A precise control over interchromophoric ordering within its crystalline frameworks^{7c} can play a key role in delineating new solid-state platform for anisotropic energy transfer processes.^{8f} Furthermore, frameworks position chromophores periodically around modular pores,9 and thus make these systems fundamentally different than stacked aromatic chromophores possessing various excited state quenching mechanisms.¹⁰ A high chromophore density, critical for efficient photon absorption in LH model system, can be achieved in a MOF. While exciton hopping among the closely spaced chromophores within these solid materials were found to be quite efficient,8 experiment probing the spectral evolution as a function of interchromophoric orientation is surprisingly rare. Difficulty in generating frameworks consisting of identical building blocks, particularly chromophoric linkers, may pose a major reason behind it. Recall the antenna complex in purple bacteria, where one kind of chromophore was engineered to generate coherent or collective property^{1a, 2} via a strong electronic coupling (~300 cm⁻¹) among the precisely positioned bacteriochlorophyll-a. This essentially produces new chromophores with a gradient in energy gap directing the sequential energy migration among the various LH complexes.1a



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Here we report topological control over the photophysical properties by probing the singlet state emissive properties of

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Electronic Supplementary Information (ESI) available: [materials, instrumentation, and procedures; characterization (NMR, PXRD, and SEM-EDS); emission spectra, TCSPC, and computation details]. See DOI: 10.1039/x0xx00000x

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Zr MOFs consisting two -based of tetrakis(4carboxyphenyl)porphyrin (TCPP)-derived linkers with different network topologies such as NU-902 (scu) and MOF-525 (ftw). We present the evolution of steady-state and time-resolved emission spectra and fluorescence lifetime as a function of interchromophoric orientation and macrocyclic ring planarity with varying framework topology. Furthermore, investigated the relative efficiency of exciton migration within a given MOF with metallated and free-base porphyrin linkers. Four MOF samples: NU-902(H2) and MOF-525(H2) consisting of free-base TCPP(H2), and NU-902(Zn) and MOF-525(Zn) consisting of zinc(II)-metallated TCPP(Zn) linkers were studied here. These samples were prepared according to literature procedure as the free-base versions.¹¹ Metalation with zinc(II) was achieved post-synthetically.^{11a} (see ESI section S3-S4).



The underlying topological networks of MOF-525 (cubic; ftw) and NU-902 (rhombic; scu) manifest the smallest porphyrin-porphyrin torsional angle of 90° and 60° respectively. Linker geometry and orientation within the frameworks were obtained via constrained DFT (CAM-B3LYP//LANL2DZ; see ESI section S5) optimization of two adjacent TCPP-M units with the smallest torsional angle, where the carboxylate (O₂C-) moieties positions with their corresponding were fixed at crystallographic coordinates. DFT optimization within the framework connectivity was necessary to affirm the position of the H-atoms and to obtain the atomic coordinates of a stable conformation (instead of the thermally allowed probable coordinates reported in the crystallographic data) of the linkers. As highlighted in Figs. 2 and SI-6, such cofacial orientation leads to interchromophoric center-to-center distance $(d_{M-M}) = 13.5$ and 10.5 Å for MOF-525 and NU-902 respectively. Furthermore, the node connectivity and symmetry of the linkers (12,4 for MOF-525 and 8,4 for Nu-902), for these topological nets, have a subtle stereochemical impact on the porphyrin ring planarity. For the *ftw* topology, the carboxylates (O-C-O) are required to be coplanar with the cubic faces that are lined up with the porphyrin macrocycle planes. This enforces the linker to adopt an energetically demanding conformation where the mesophenyl groups need to be non-planar to both the carboxylate and porphyrin planes; these constrains eventually lead to a nonplanar porphyrin. On the contrary, the NU-902 requires the carboxylate to be at ~55° angle to the macrocycle allowing the linker to adopt a stable conformation, where the carboxylate and meso-phenyl are nearly coplanar.

Next, we examined how these structural features critically impact the evolution of their spectroscopic signatures. Fig. 3 highlights the steady state emission and excitation spectra

collected in gas phase under argon [to eliminatentine solvatochromic effect]. Emission spectra of MOFS255(H2)34A NU-902(H2) show different extent of red shift along with different relative intensity of the $Q_{0,0}$ and $Q_{0,1}$ bands compared to a free TCPPOMe(H2) linker in dichloromethane solvent. We attribute this red-shifted Q band emission to different degree of excitonic coupling among the closely placed chromophores as a function of their orientation. For example, in MOF-525, a dominant coupling should stem from one of the Q_x or Q_y derived transition dipole of adjacent chromophores aligned at 90° (**Fig. 2**; *vide infra*). Likewise, a stronger coupling can be expected for NU-902 among the adjacent chromophores that are positioned at 10.5 Å with 60° torsional angle.



The difference in relative intensity of the $Q_{0,0}$ and $Q_{0,1}$ derived vibronic emission bands are stemming from the varying degree of ring planarity adopted by the TCPP linker within the two topological networks. The degree of ring planarity impacts the symmetry and hence on the allowance of the lowest energy electronic transitions. Considering excitation spectra as complementary to an electronic absorption spectra, a clear difference in the intensity and transition energies for various vibronic transitions [contributing to their lowest emission bands ~730 nm] can be observed. To understand how the interchromophoric interactions impact their spectral evolution, we have computed the electronic transitions via TD-DFT method (CAM-B3LYP//LANL2DZ; see ESI section-S5) on their corresponding DFT-optimized structures shown in Figs. 2 and SI-6. Computed electronic transitions for NU-902(H2) and TCPP(H2) are summarized in Fig. 3c and represented with oscillator strengths and extinction spectra. These data clearly suggest sizable red shifted transitions for the dimer in both the Q and Soret band regions, and highlight appearance of new

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transitions due to exciton splitting. Frontier molecular orbitals of these dimers indeed show a sizable electron density shared by the two porphyrin units (see **Fig. SI-7**). The zinc(II) metallated MOFs, however, show subtle difference in that the degree of redshift relative to the free TCPPOMe(Zn) is more pronounced and the spectral evolutions for MOF-525(Zn) and NU-902(Zn) are more similar (**Fig. SI-8**) than that observed for the free-base samples (**Fig. 3a**). Such spectral evolution is plausible due to a better degree of ring planarity and higher symmetry of macrocycles resulting in better excitonic coupling that the free-base variant.

To gain insight into the effect of these spectral features on their corresponding excited state properties, we studied transient fluorescence decay along with the evolution of timeresolved fluorescence spectra for both the free base and zincmetallated MOF samples. Summarized in Fig. 4 (and Figs. SI-10, 11) are the gas phase transient fluorescence decay profiles as well as time-resolved emission spectra collected under argon. In general, the fluorescence lifetime of the MOF samples are significantly shorter compared to the corresponding free linkers in solution and follow a trend with the relative redshifts found in their steady-state emission spectra (Figs 3, SI-8). For example, compared to a free TCPPOMe(H2) linker (τ = 9 ns), the fluorescence lifetimes for MOF-525(H2) and NU-902(H2) were found to be ~5.6 and 4.6 ns (considering only the major component). We attribute these shorter lifetimes to their diminished electronic transition energy-gaps (S₁-S₀)¹² stemming from the interchromophoric interaction: NU-902(H2) has stronger excitonic coupling than MOF-525(H2) to render a low $Q_{0,1}$ transition, which, in turn, shorten the excited state lifetime.



The fluorescence lifetime for the corresponding zinc(II) metallated MOF samples follow an identical trend as TCPPOMe(Zn)>MOF-525(Zn)>NU-902(Zn); the difference of emissive life-time between a zinc-metallated MOF sample and the free TCPP(Zn) linker is discernibly larger relative to that of a corresponding free-base system. We attribute this to a better chromophoric interaction in the metallated samples as seen for their steady-state emission spectra (**Fig. SI-8**). To gain deeper

insight, we examined wavelength dependent dynamics of the emissive states with time-resolved emission speetra. For the free-base MOF samples, the emissive state decays to both the vo and v1 vibrational levels of the ground state are followed with identical time constants (Figs 4b, SI-10) indicating that interchromophoric interactions within the constrained conformations provided by the frameworks do not alter the transition probability to both the vibrational levels of the ground state. Thus the evolution of their time-resolved emission spectra mirrors their steady-state spectra (Figs. 4b, 3a). However, for NU-902(Zn) and MOF-525(Zn), the dynamics of the emissive state radiative decay to the v_0 and v_1 vibrational levels of the ground state are different (Fig. SI-10). With a faster emissive decay to the lower energy vo vibrational level of the ground state, the evolution of time-resolved emission spectra are non-identical to their corresponding steady state spectra (Figs. 4d, SI-8, 11). This observation can be rationalized based on the fact that an enhanced chromophore symmetry within these constrained framework geometries may have facilitated a better Franck-Condon overlap between two vo vibrational levels of emissive excited and ground electronic states. This assertion would be associated with manifestation of an increased $Q_{0,0}$ intensity for the MOF sample relative to that of the free TCPP(Zn) (Figs. SI-8a, SI-13c)

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To verify if these spectroscopic features are indeed manifested by the chromophore cofacial dimers lined at the closest proximity, we spectroscopically studied PCN-222(M) [M=H2, Zn(II); *csq* net with identical molecular formula as that of NU-902(H2)].^{11b} As shown in **Fig. SI-12**, PCN-222 consists of identical TCPP(H2) linker and Zr_6 node forming triangular and hexagonal channels. Any two of the three TCPP linkers within the triangular channel possess spatial orientation identical to that present in NU-902 (**Figs. 2, SI-12**). Both steady state and transient emissive spectroscopic features for PCN-222 were found to be essentially identical to the NU-902 samples (**Fig. SI-13**).

With these spectroscopic data in hand, we proceeded to study the efficiency of singlet state energy transfer processes within some of these MOF samples via the amplified emissive quenching experiments. We installed ferrocene (Fc) -based Fc-COO⁻ quencher, at various Fc/por doping ratio, using a wellestablished solvent assisted ligand incorporation (SALI; see ESI section S7) method at the Zr₆-oxo node via a robust Zr^{IV}carboxylate linkage.¹³ Analysis of the emission quenching data (ESI section S7) as a function of Fc/por ratio indicates that the number of chromophores the exciton visits within its lifetime are 5 for NU-902(H2) and 4 for NU-902(Zn) with corresponding absolute displacement estimated to be 2.5 and 2 linkers respectively. The number of hops made by the exciton is ~6 for NU-902(H2) and 4 for NU-902(Zn) with estimated hopping times of 4630/6 = 770 ps and 410/4 = 100 ps, respectively. Furthermore, considering the saturation emission intensity at 0.37 and 0.45 of Fc-COO⁻ doping level (ESI section S7), we estimated electron transfer rate from Fc to porphyrin to be at least $\sim 0.4 \times 10^9 \text{ s}^{-1}$ for NU-902(H2) and $\sim 4 \times 10^9 \text{ s}^{-1}$ for NU-902(Zn). These metrics are in good agreement with the related 5,15-dipyridyl(porphinato)zinc(II) based MOF.8f The transient

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emission decay profiles of the Fc-COO⁻ doped NU-902(H2) and NU-902(Zn) samples (**Fig. 5**) also correlate that a better exciton migration efficiency in NU-902(H2), possibly due to a stronger oscillator strength of the Q band and a better overlap between the absorption and emission spectra compared to the metallated MOFs (**Fig. SI-14**).



In summary, with the help of computational and experimental data, we found that the singlet state emissive spectral features of MOFs are inherently different and a function of their underlying framework topology. In these solidstate samples, framework topology dictates the interchromophoric orientation and interactions. Stronger interchromophoric interaction leads to more red shifted spectra (smaller S1-So energy gap) with faster emissive state radiative decay. Ability to modulate the corresponding emissive state lifetimes in LH model systems should enable to control the number of exciton hopping and effective exciton displacement. Even with identical building blocks, chromophore ring planarity may vary due to the network symmetry imposed by the underlying frameworks to manifest modified emission spectra. Furthermore, for a given topological network, framework consisting of less symmetric linker manifests more exciton hopping. The findings reported here thus underscore that topological control over the photophysical properties of MOFs can play a critical role in processes relevant for light harvesting utility.

We gratefully acknowledge the support from SIU Carbondale start-up funds and the State of Illinois. PD acknowledges the Ralph E Powe Jr. Faculty Enhancement Award, Oak Ridge Associate University, and SNW acknowledges NSF-REU fellowship. We acknowledge Prof. Qingfeng Ge, SIUC for providing access to the computational facility.

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