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Dynamic electric field alignment of metal-organic framework microrods

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ABSTRACT: Alignment of Metal Organic Framework (MOF) crystals has previously been performed via careful control of oriented MOF growth on substrates, as well as by dynamic magnetic alignment. We show here that microrod crystals of the MOF NU-1000 can also be dynamically aligned via electric fields whilst suspended in bromobenzene, giving rise to rapid electrooptical responses. This method of dynamic MOF alignment opens up new avenues of MOF control which are important for integration of MOFs into switchable electronic devices as well as in other applications such as reconfigurable sensors or optical systems.

Metal-organic frameworks, which are crystalline materials comprising of inorganic nodes linked by organic ligands, are of significant research interest due to their flexible choice of linkers and metals which afford them wide-ranging applications[1-3] such as in optics, sensing, electronics, gas separations and energy storage.

It should also be noted that as most MOFs possess lattice anisotropy along different crystallographic axes, their corresponding chemical and physical properties also significantly differ along different crystallographic directions. Therefore, to fully exploit directional functionality of MOFs, it is important to be able to control MOF particle orientation. However, as MOF materials are typically synthesized as loose colloidal powders, it is challenging to impose and integrate particle orientational control into their utilization. Research in this area has consequently focused on growth of MOF crystals on various substrates, to favour selective directional growth.[4-6] However, this is time-consuming, and significant care must be taken to control crystal growth. Furthermore, the growth conditions for one type of MOF cannot simply be applied wholesale to other MOFs, with considerations of MOF-substrate lattice matching and interfacial physicochemical interactions complicating the widespread application of this approach.[7] Significantly, this approach renders the MOF orientation static, hindering the use of MOFs in applications requiring dynamicity, such as in stimuli-responsive devices, whereby the MOFs can reorient themselves under changing conditions. Given the vast applicability of MOFs, the ability to control MOF alignment in a dynamic fashion will have significant implications for many areas.

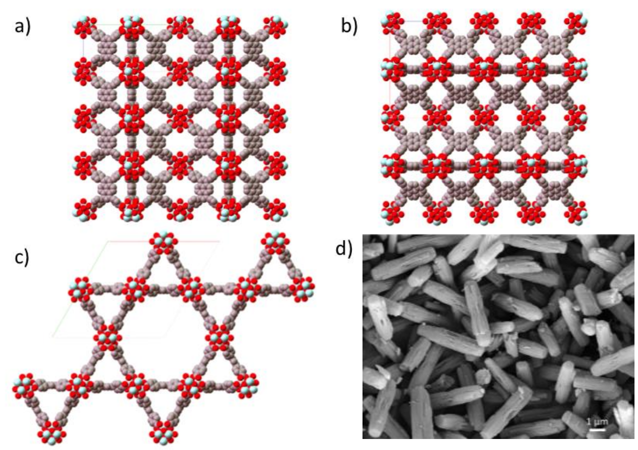

Figure 1. a-c) View of NU-1000 lattice along the *a*, *b* and *c* crystallographic axes respectively, showing the lattice anisotropy; d) Scanning electron micrograph of NU-1000 microrods where the shape anisotropy of the particles can be clearly observed.

The long range molecular order imposed by the MOF lattices, and their tuneable physicochemical properties, also render MOFs especially attractive for use in electronic devices.[8] E-field control of MOFs is therefore particularly desirable and there are emerging reports of external E-field MOF manipulation. Examples current driven synthesis of ZIF-8,[9] field-driven rotation of MOF ligands,[10-11] as well as the E-field induced polymorph switching of ZIF-8[12] and MIL-53.[13-15] Reports pertaining to control of MOF crystal assembly include their electrophoretic deposition into electroactive thin films,[10, 16] and the assembly of polyhedral ZIF-8 microparticles into locked chains under an alternating E-field,[17] whereby the flat particle facets allowed for inter-particle facet-to-facet adhesion through Van der Waals forces, as the alternating electric field polarized the electrostatic double layer. Further to this, Choi *et al.* showed that suspensions of $Cu_3(BTC)_2$ in silicone oil possessed electrorheological properties, whereby application of an electric field leads to particle chaining within $Cu_3(BTC)_2$ suspensions.[18] Nevertheless, reports of electric field control of MOF particle assembly are still extremely sparse, and have not focused on switchable control of MOF orientation despite the promise this area offers.

NU-1000, a zirconium-based MOF, possesses an anisotropic lattice, comprising of 8-connected $Zr_6(\mu_3\text{-}OH)_4(\mu_3\text{-}O)_4(OH)_4(OH_2)_4$ nodes linked by tetratopic 1,3,6,8-tetrakis(*p*-benzoate)pyrene (TBAPy) ligands.[19-20] 31 Å hexagonal channels and 12 Å triangular channels are oriented along the c-axis of NU-1000 crystals (Figure 1) and smaller 10 Å pores perpendicular to these channels, resulting in anisotropic molecular diffusivity[21] and photophysical properties for NU-1000.[22]

We have previously shown that magnetized NU-1000 could be dynamically aligned via magnetic fields.[22] However, the use of electric fields for MOF alignment would significantly widen the scope for device integration as it is simpler and more practical to implement for many applications. E-fields also have a greater dynamic range of field strengths and are easier to localize, avoiding cross-talk or interference within devices. Here we demonstrate for the first time, the utilization of electric fields to dynamically and reversibly control NU-1000 alignment. NU-1000 was selected for these investigations, due to its lattice and particle shape anisotropy, high chemical and thermal stability, large specific surface area, scalability of synthesis,[23] as well as its potential uses in catalysis and as modifiable functional substrates.[24]

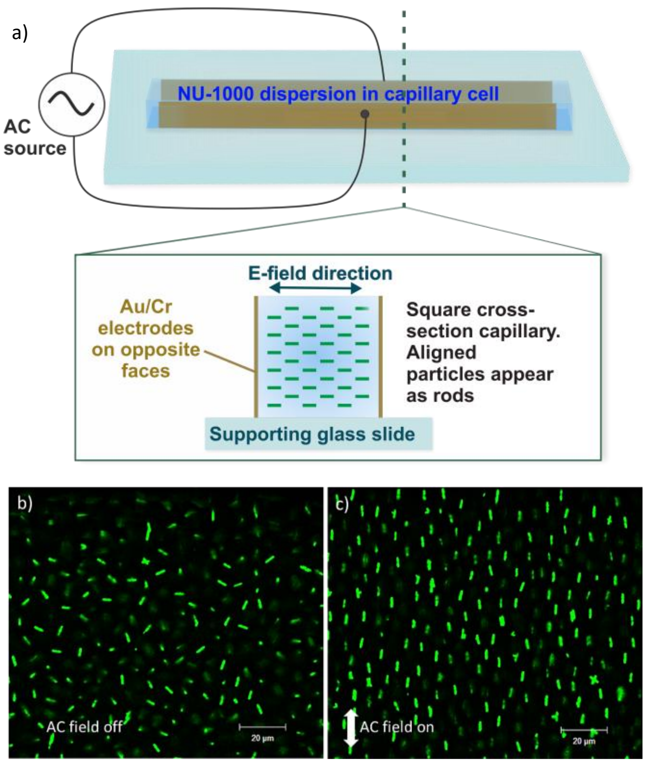

Figure 2. a) Illustration of a glass capillary set-up where the $NU\text{-}1000_{Si}$ suspension in the cell is exposed to an alternating electric field perpendicular to the viewing direction (top) and cross-sectional view of the glass capillary set-up (bottom); b) Confocal microscope images of $NU\text{-}1000_{Si}$ suspensions in bromobenzene, without E-field and showing random particle orientation and c), in the presence of 500 Hz, 37.5 $V\cdot mm^{-1}$ peak-to-peak E-field showing particles aligned along the E-field.

NU-1000 microcrystals were synthesized and activated in accordance to literature procedures.[23] This synthesis led to size monodisperse NU-1000 microrods, although we also observed the occurrence of some cross-shaped particles, presumably due to NU-901 co-crystallization and subsequent NU-1000 growth on the NU-901 nodes (Figure S1).[20] To improve the dispersibility of the NU-1000 microcrystals in various organic solvents, the NU-1000 was functionalized with trimethoxy(octadecyl)silane (TMODS) to afford $NU\text{-}1000_{Si}$ (Figure S2 and S3). IR spectroscopy shows the presence of an IR absorption band at 3674 cm^{-1} corresponding to terminal -OH groups (from the zirconia clusters) on the NU-1000.[19] The $NU\text{-}1000_{Si}$ obtained after functionalization with TMODS showed a decrease in the band at 3674 cm^{-1}, consistent with expectations as well as the occurrence of overlapping bands from 1130 to 930 cm^{-1}, attributed to Si-O-Si and Si-O-Zr bonds (Figure S4). Inductively coupled plasma-mass spectrometry (ICP-MS) of $NU\text{-}1000_{Si}$ showed the ratio of Zr : Si to be 1: 1.39, or 8.3 Si per Zr_6 node. These findings can be explained by silyl ethers on the Zr_6 nodes further reacting with TMODS to form siloxy bridges. Powder X-ray diffraction (PXRD) also indicates that the $NU\text{-}1000_{Si}$ retains its crystalline framework structure after silanization (Figure S5).

Rectangular and square cross-section capillary cells were prepared whereby opposite sides of the cells were coated with Au/Cr via e-beam deposition and connected to an AC source through silver and electrical wires (Figure 2a). The capillaries were filled with suspensions of $NU\text{-}1000_{Si}$ in bromobenzene. Bromobenzene was selected as its density (1.474 g/mL at 25 °C) was relatively closely matched with that of $NU\text{-}1000_{Si}$, giving stable suspensions across the timescale of weeks. Furthermore, the low dielectric constant of bromobenzene (ε = 5.19) affords relatively large inverse Debye screening lengths $1/\kappa$ as the low electrolyte content in non-polar solvents[25] facilitates large interparticle separations, which may allow for more rapid particle alignment. However, as the NU-1000 scaffold is expected to have a high refractive index (different from the averaged refractive index of the MOF lattice and the pore-filling fluid) due to its zirconia nodes, it was not possible to find an index-matched solvent for minimization of van der Waals interactions and avoidance of light scattering effects. Nevertheless, by minimizing the thickness of the focal plane through decreasing the pinhole size, we were able to study the particle dispersions via confocal microscopy.

Conveniently, the pyrene-based ligand in NU-1000 acts as a fluorophore, causing NU-1000 to absorb 405 nm radiation and fluoresce at 470 nm. This allows for confocal microscopy of $NU\text{-}1000_{Si}$ suspensions with no need for additional functionalization with a fluorescent dye. The $NU\text{-}1000_{Si}$ crystals show random orientation and thermal movement in the bromobenzene-based suspension, and are well separated by electrostatic repulsion, preventing their aggregation or gelation (Figure 2b).

The $NU\text{-}1000_{Si}$ particle suspensions show some order in their particle arrangement, in spite of thermal and Brownian motion (Figure S6). This is reminiscent of the colloidal plastic crystals or rotator phases described by van Blaaderen's group,[26] whereby interparticle electrostatic repulsions afford positional order but not orientational order as the microrods rotate randomly around in their positions. However, the presence of the cross-shaped $NU\text{-}1000_{Si}$ particles appeared to disrupt the positional order observed here. Upon exposure to an alternating electric field, however, the NU-1000$_{Si}$ microrods rapidly align along the electric field direction (Figure 2c). Under these conditions, we did not observe particle chaining of NU-1000$_{Si}$. Like in the case of electro-responsive SiO_2-based plastic crystals,[26] the observed interparticle repulsion prevents the particles from aggregating. Furthermore, as the tips of the NU-1000$_{Si}$ microrods are not perfectly flat, and the microrods surfaces were sterically stabilized by octadecylsiloxy groups, Van der Waals based facet-to-facet attraction at the tips is expected to be relatively low.

To determine the electroresponse rate and extent, electrooptical measurements were carried out, using a polarized optical

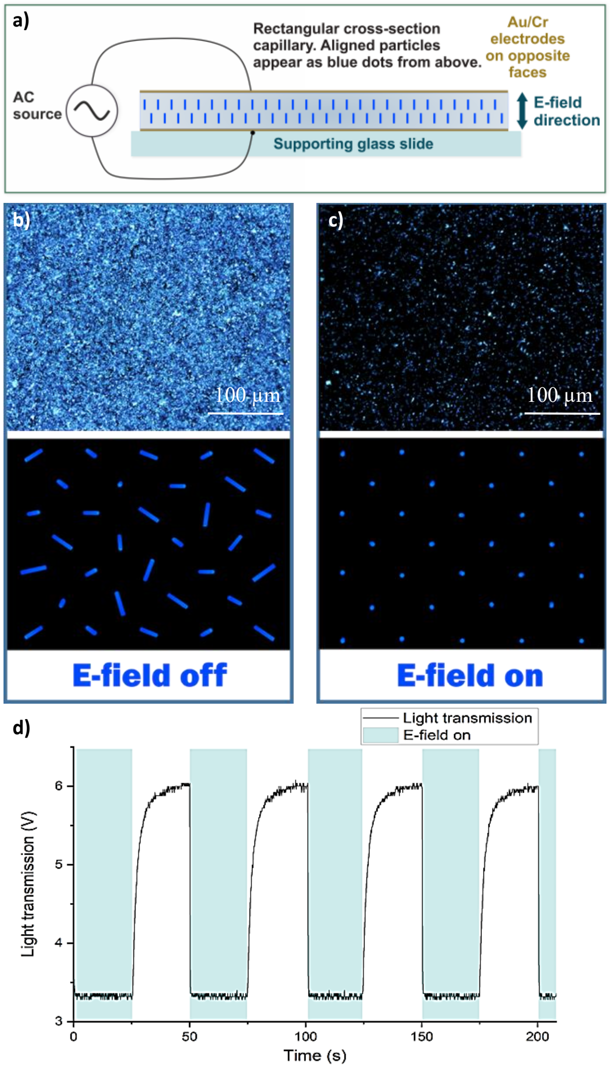

Figure 3. a) Cross-sectional view of rectangular capillary used in electrooptical measurements. Electrical alignment of particles occurs vertically; b) top and bottom, respectively: bright polarized optical microscope (POM) image of 2 wt% NU-1000$_{Si}$ suspension in bromobenzene showing transmission of light due to crystal birefringence and an illustration depicting the random orientation of the crystals when E-field is off; c) top and bottom, respectively: dark POM image of the same suspension showing decreased light transmission due to NU-1000$_{Si}$ alignment along the alternating E-field, perpendicular to the plane of the paper and illustration depicting the particle alignment.; d) Electrooptical response of the suspension - light transmission under alternating E-field (100 V·mm^{-1} peak-to-peak, 500 Hz).

microscope and a photodetector (Thorlabs PDA100A Si Amplified Detector) to measure light transmission through the cell. NU-1000 crystallizes in the hexagonal space group *P6/mmm*[27,19] and is uniaxially birefringent. When viewed through crossed polarizers on an optical microscope, the particles appear blue against a dark background (Figure 3a). When the electric field is off, the NU-1000$_{Si}$ microrods are randomly oriented and undergo Brownian motion. Turning on the alternating electric field results in the rapid vertical alignment of the microrods (Figure 3a, particles appearing as blue dots) perpendicular to the viewing plane and a decreased transmission of light, whereby the long axis of the microrods aligns with the direction of light transmission and the cross-sectional area of crystals for light transmission decreases (Figure 3b,c). This is similar to previous observations of liquid crystalline niobate nanosheets where light propagation is minimized during particle alignment.[28] By plotting the changes in light transmission against time and E-field switching, we can determine the response rate and its extent. When the E-field is switched off, the particles relax slowly back into their random orientations, and the light transmission goes back to a maximum, as shown by the curved, unshaded sections of the graphs (Figure 3d).

The E-field alignment of NU-1000$_{Si}$ is frequency dependent, with the most rapid alignment occurring at 500 Hz (0.1 s) for NU-1000$_{Si}$ particles suspended in bromobenzene (Figure S7). The E-field induces polarization of NU-1000$_{Si}$ and the particles

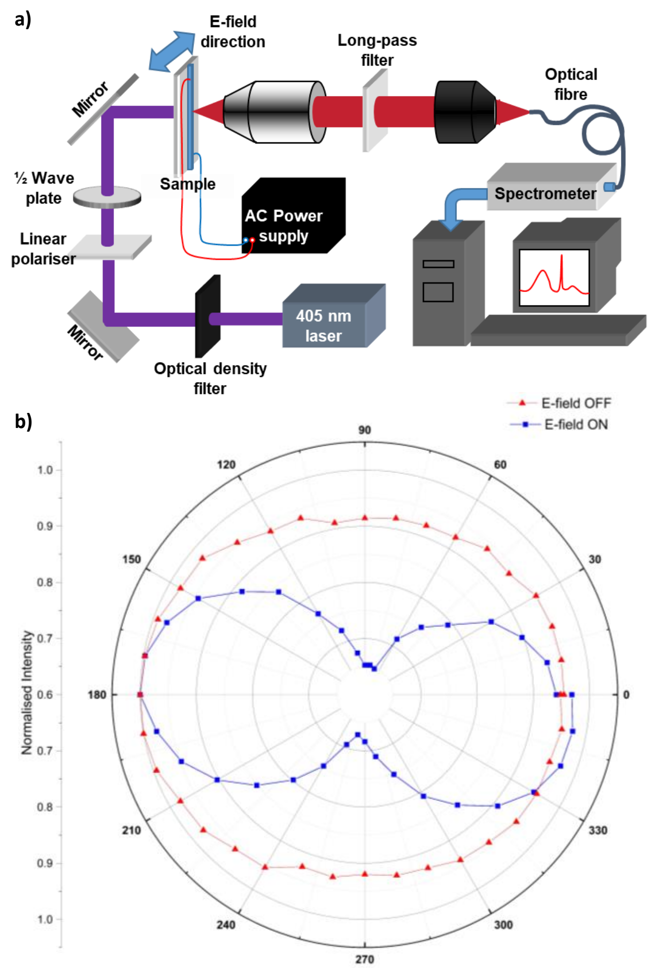

Figure 4. a) Fluorescence response study set-up; b) Azimuthal plot of fluorescence intensity response of NU-1000$_{Si}$ particles in bromobenzene when in a 500 Hz 100 V·mm^{-1} peak-to-peak E-field (blue) and when the field is off (red). Electric field orientation is at 0°.

align their axes of greatest polarizability along the field direction.[29] Particle polarization is induced through various mechanisms in an alternating electric field, with the mechanism dependent upon the field frequency and the particle material.[30,31] In this case, the low frequency suggests that the alignment process most likely takes place through Maxwell-Wagner-Sillars and O'Konski interfacial polarization.[32-35] In particular, we hypothesize that ions present within the NU-1000$_{Si}$ channels and in the electrical double layer on the external MOF particle-solvent interface undergo electromigration due to the imposed E-field.[36] These ions may result from the presence of adsorbed water and polar groups such as Zr-OH and Si-OH at the MOF-solvent interface[37-38] as well as from the sample preparation. Indeed, we found that the NU-1000$_{Si}$ particles possess negative zeta potentials when dispersed in bromobenzene (Table S1). As the MOF channels run along the C-axis along the length of the microrods, induced dipoles arising from ion migration along the 1-D MOF channels cause E-field alignment of the NU-1000$_{Si}$ microrods. Further, since physisorption measurements of NU-1000$_{Si}$ showed it has a high specific surface area of 916 $m^2 g^{-1}$ and pore volume (Figures S8 and S9, Table S2), interfacial polarization effects are expected to be high.

We previously showed that magnetically aligned NU-1000/Sylgard 184 composites exhibited a fluoresence response which was dependent upon the angle of linearly polarized excitation.[22] This angular dependence arises from the lattice anisotropy of NU-1000, as the pyrene-based TBAPy ligands are oriented along the C-axis (Figure 1) and hence display anisotropic absorbance of linearly polarized excitation. Drawing upon this, we carried out fluorescence response studies on NU-1000$_{Si}$ suspensions. The samples were irradiated at normal incidence to the sample plane with 405 nm linearly polarized excitation, and their photoluminescence anisotropy determined. A half-wave plate was used to adjust the polarization angle of the incident light, and measurements were taken at 10° intervals. (Figure 4a) The integrated fluorescence intensity, normalized to its maximum value, is shown by the azimuthal plot in Figure 4. When the NU-1000$_{Si}$ particles are electrically aligned, the photoluminescence response is significantly dependent upon the polarization angle of the excitation relative to the E-field and MOF alignment direction. The highest fluorescence intensity is observed when the polarization angle of incident light is 0° to the E-field direction whereas the fluorescence minima occurs when the angle is 90°, in accordance to expectations.

In conclusion, we have demonstrated the dynamic alignment of NU-1000$_{Si}$ through electric-field switching, and shown reversible electrooptical responses as well as orientationally-dependent fluorescence response of the NU-1000$_{Si}$ dispersions. Such an approach is expected to be applicable to a wide variety of MOFs, as their high surface areas should allow for interfacial polarization and E-field alignment. As such, this work is expected to open up possibilities for the development of switchable MOF assemblies and devices. Future work will focus on the detailed investigation of the parameters required for applying E-field alignment to other MOFs, such as the effect of MOF network topology and pore structure, ion concentration, particle surface functionalities and solvent selection on their E-field alignment.

ASSOCIATED CONTENT

Supporting Information

Experimental details and characterization results are included in the ESI. A video showing E-field induced alignment of NU-1000$_{Si}$ in bromobenzene as viewed through a confocal microscope where individual NU-1000$_{Si}$ rods can be seen (100 V·mm^{-1} peak-to-peak, 1 kHz), and a video showing electrooptical switching of NU-1000$_{Si}$ in bromobenzene (100 V·mm^{-1} peak-to-peak, 500 Hz) viewed through crossed polarizers on an optical microscope are also included.

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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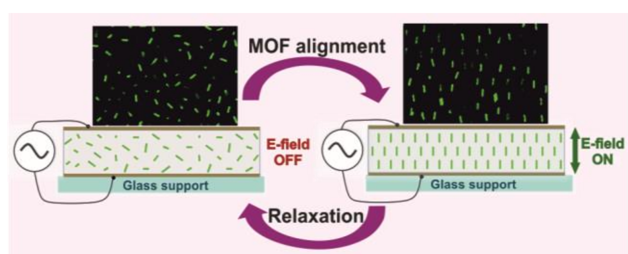

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