ABSTRACT: We demonstrate the formation of both metallo-organic crystals and nanoscale films that have entirely different compositions and structures despite using the same set of starting materials. This difference is the result of an unexpected cation exchange process. The reaction of an iron polypyridyl complex with a copper salt by diffusion of one solution into another resulted in iron-to-copper exchange, concurrent ligand rearrangement, and the formation of metal–organic frameworks (MOFs). This observation shows that polypyridyl complexes can be used as expendable precursors for the growth of MOFs. In contrast, alternative depositions of the iron polypyridyl complex with a copper salt by automated spin coating on conductive metal oxides resulted in the formation of electrochromic coatings, and the structure and redox properties of the iron complex were retained. The possibility to form such different networks from the same set of molecular building blocks by “in solution” versus “on surface” coordination chemistry broadens the synthetic space to design functional materials.
by the formation of a coordination polymer consisting of the polypyridyl ligand and copper cations. In contrast, alternative spin coating of the same iron polypyridyl complex with copper nitrate on fluorine-doped tin oxide (FTO) resulted in electrochromic coatings. Their electrochromic activity originates from the iron polypyridyl complex. The free pyridine moieties of the polypyridyl ligands are coordinated to the copper cations, forming a dense network of iron complexes. This network stabilizes the iron complexes, as cation exchange was not observed, even after prolonged exposure to a solution containing an excess of copper salt.

Crystals were obtained by slow diffusion of solutions into one another at room temperature. We used a thin tube (ø = 5 mm) containing three layers, with the top and bottom layers consisting of solutions of complex 1 or Cu(NO₃)₂ and the layer in the center being a cosolvent. During the reaction, the color of the solution changed from purple to colorless. These coordination organic networks (SolCONS) were isolated after 20 days by centrifugation and washed with acetonitrile (ACN) and ethanol. Two different solvent combinations were used and resulted in the same crystallographic structures and morphologies, but with slightly different dimensions.

SolCON-A was formed by the reaction of complex 1 (CH₂Cl₂/MeOH, 1:1 v/v) with Cu(NO₃)₂·3H₂O in ACN in a molar ratio of 1:2. CH₂Cl₂/MeOH/ACN (0.5:0.5:1 v/v/v) was used as a cosolvent in the center. SolCON-B was obtained by using ACN as the solvent for complex 1 and N,N-dimethylformamide (DMF) as the solvent for Cu(NO₃)₂·3H₂O. ACN/DMF (1:1 v/v) was used as a cosolvent in the center (Figure 1). Scanning electron microscopy (SEM) analysis revealed the formation of crystals that have the appearance of a parallelpeped (Figure 1, Chart 1). Although these crystals were uniformly shaped, their dimensions varied. For SolCON-A the size distribution was 2.1 ± 0.9 μm (~50 crystals), and for SolCON-B sizes were between 1 and 4 μm (~50 crystals). In addition, larger crystals of 38–70 μm (~10 crystals) were also observed for SolCON-B (Figure S1). The different solvent combinations did not affect the overall crystal morphology, as is sometimes observed.

Single-crystal X-ray analysis of SolCON-B showed the formation of a MOF based on copper cations and the ligand of complex 1 (Figure 1, Chart 2). The formation of the framework involved ligand transfer from complex 1 to the copper salt. The three-dimensional framework is formed by mono- and bidentate binding of copper centers to the pyridine moieties of the ligand. The ligands are coordinated in square-pyramidal fashion around the copper centers. The Irving–Williams series indicates that the relative stability of the copper complexes is expected to be larger than that of the iron complex 1. Although structurally different, both coordination complexes have six metal–pyridine bonds. The N₃₋₋Cu²⁺ bonds are known to be stronger than Npyr−Fe²⁺.51 Two nitrate counteranions are present in the asymmetric unit, and hydrogen bonding is observed between the oxygen atom of NO₃⁻ and hydrogen atoms of the polypyridyl ligand. The nanobeam electron diffraction (NBED) patterns of SolCON-A consist of sharp spots that match with the corresponding zone-axis patterns calculated from the refined structure of SolCON-B, demonstrating that these MOFs have very similar crystallographic structures (Figure 1, Chart 3, and Figure S2). The iron center of complex 1 is coordinately saturated, and therefore, it is highly likely that the metal cation exchange involves ligand dissociation prior to the formation of the MOFs.52 The vinlypyridyl moieties of complex 1 are not essential for the cation exchange, as shown by the reaction of [Fe(bpy)₃][PF₆]₂ (lacking the vinylpyridyl moieties) with Cu(NO₃)₂ (40 equiv) in ACN. We observed the disappearance of the typical red color associated with this iron complex within 60 h.53

To demonstrate the differences between bulk crystallization and on-surface chemistry, a thin film (SurCON) was prepared by layer-by-layer (LbL) deposition of solutions containing complex 1 and Cu(NO₃)₂ (Figure 2). With this approach, complex 1 retains its structure and electrochromic properties. SurCON was assembled on FTO on glass (2 cm × 2 cm) using automated spin coating and solutions of Cu(NO₃)₂·3H₂O (4.0 mM in ACN) and complex 1 (0.6 mM in CH₂Cl₂/MeOH, 1:1 v/v). This deposition sequence was repeated 18 times. The SurCON was coated with a thin layer of platinum and milled using a focused ion beam (FIB) microscope (Figure 2, Chart 1). The transmission electron microscopy (TEM) image of a cross section of SurCON shows a homogeneous film having a thickness of ∼178 nm. Energy-dispersive X-ray spectroscopy
con as cross-linkers (Figure 2, Chart 2B). Two characteristic bands intensities of the MLCT bands. The time required to reach with the satellite bands at 941 nm. Plotting the absorption intensity (λ) versus the number of deposition cycles indicated linear growth with a half-wave potential (V) upon oxidation of Fe²⁺ to Fe³⁺. This reversible process separated 310 mV at a scan rate of 100 mV/s. The color of the electrochromic complex bound by two pyridine groups. The Npyr/Fe ratio of 11.9 is in excellent agreement with the expected ratio for complex Cu(NO₃)₂·3H₂O (4.0 mM in ACN) for 3 days did not result in ligand transfer (Figure S4). Clearly, the formation of a network containing both the copper salt and complex 1 enhances its stability.

In conclusion, the reactions demonstrated here are two examples of coordination-based polymerization processes: (i) metal–ligand exchange followed by crystallization versus (ii) on-surface deposition. The composition of the assemblies is controlled by the applied method. We have shown that iron polypyrrolid complexes can be used as sacrificial precursors for the formation of MOFs by slow diffusion of solutions. The on-surface polymerization is much faster, which prevents the metal–ligand exchange.

Fast mixing of solutions of iron complex 1 and Cu(NO₃)₂·3H₂O resulted in a network without metal cation exchange, as shown by XPS, SEM, and EDS measurements (Figure S5). These observations suggest the formation of a kinetic product, whereas a thermodynamically favorable product is obtained by

(EDS) mapping clearly indicates the uniform distribution of both the iron and copper cations. UV–vis spectra recorded for different numbers of deposition cycles showed the broad metal-to-ligand charge transfer (MLCT) bands related to complex 1 at λₘₐₓ₁ ≈ 458 nm and λₘₐₓ₂ ≈ 596 nm (Figure 2, Chart 2A). An intense π–π* transition band of the ligand was also present at λₘₐₓ ≈ 333 nm. Plotting the absorption intensity (λₘₐₓ ≈ 596 nm) versus the number of deposition cycles indicated linear growth with retention of complex 1.

X-ray photoelectron spectroscopy (XPS) data for SurCON confirmed the presence of iron complex 1 and copper cations as cross-linkers (Figure 2, Chart 2B). Two characteristic bands for Fe²⁺ are present at 708 eV (2p₃/₂) and 720 eV (2p₁/₂). The Nₚyr/Fe ratio of 11.9 is in excellent agreement with the expected ratio for complex 1 (Nₚyr/Fe = 12). The bands for Cu²⁺ are observed at 935 eV (2p₃/₂) and 955 eV (2p₁/₂) along with the satellite bands at 941–945 and 962–965 eV. The observed Cu/Fe ratio (~2.7) indicates the formation of a fully formed network (Cu/Fe = 3) in which the copper centers are bound by two pyridine groups.

Electrochemical measurements unambiguously confirmed the presence of the electrochromic complex 1 (Figure 2, Chart 3). Cyclic voltammograms (CVs) showed reversible one-electron redox processes as expected for the Fe⁵⁺/³⁺ couple with a half-wave potential (E₁/₂) of 1.1 V and a peak-to-peak separation of 310 mV at a scan rate of 100 mV/s. The color of the SurCON changed from gray (at 0.4 V) to colorless (at 1.8 V) upon oxidation of Fe⁵⁺ to Fe³⁺. This reversible process could be monitored using spectroelectrochemical (SEC) measurements (Figure S3). The changes in the oxidation states were accompanied by variations in the absorption intensities of the MLCT bands. The time required to reach 90% of the maximum transmittance (ΔT ~ 40%) was ~2.1 s. The switching stability was indicated by 250 redox cycles with >80% retention of the initial ΔT. The coloration efficiency (CE) was 148 cm²/C. SurCON is densely packed, as indicated by the molecular density of ~1.1 × 10⁻⁴⁰ molecules/cm³ for a charge density (Q) of 1.77 mC/cm². Exponential and linear dependences of the anodic and cathodic peak currents on the scan rate and square root of the scan rate, respectively, were observed, indicating a redox process controlled by diffusion. The calculated diffusion coefficients (D) ≈ 3.37 × 10⁻³⁹ cm² s⁻¹ (oxidation) and ~3.64 × 10⁻⁹ cm² s⁻¹ (reduction) are similar and derived from the Randles–Svcek equation. SurCON is remarkably stable, as no cation exchange was observable by UV–vis spectroscopy and electrochemical measurements. Immersion of SurCON in a solution containing Cu(NO₃)₂·3H₂O resulted in a network without metal cation exchange, as shown by XPS, SEM, and EDS measurements (Figure S5).
slow diffusion of the solvents. Reacting a palladium salt (instead of a copper salt) with the iron polypyridyl complex in solution (by diffusion or fast mixing; Figure S6) did not result in metal–ligand exchange.55

On-surface polymerization was observed by us with palladium salts for the formation of electrochromic coatings without metal cation exchange.16,17,32,34,35,56 Forming such coatings with copper rather than palladium salts is advantageous because of the lower toxicity and cost. The use of the same complex resulted in similar properties (i.e., coloration efficiencies, maximum transmittance, and switching times) regardless of the applied salts.32,34,35,56 Others have reported the formation of related coordination structures based on terpyridine iron complexes and copper salts in solution and on surfaces.29,36,37 No exchange of the iron and copper cations has been reported. The previous finding with palladium chemistry and the above-mentioned reports by Constable, Housecroft, Gupta, Mondal, and Zharnikov highlight that our example of divergent coordination chemistry is rare and can offer new opportunities in the molecular engineering of functional materials.

Figure 2. Characterization and electrochromic properties of SurCON. Chart 1: (A) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image showing a cross section of a SurCON sample. (B, C) EDS elemental map showing the distribution of iron and copper metals. Scale bar: 100 nm. Chart 2: (A) Ex situ absorption spectra recorded during the formation of the film. FTO/glass was used for the baseline (black). Inset: Absorbance of the metal-to-ligand charge transfer (MLCT) band ($\lambda_{max} = 596$ nm) vs the number of deposition cycles. (B) X-ray photoelectron spectroscopy (XPS) spectra. Chart 3: (A) Photographs of the colored (0.4 V, Fe$^{2+}$) and bleached (1.8 V, Fe$^{3+}$) states using an electrolyte solution of 0.1 M TBAPF$_6$ in ACN. Additional details are shown in Figure S3. (B) Cyclic voltammograms (CVs) recorded at a scan rate of 100 mV/s. (C) Absorption spectra showing the reduced (gray) and oxidized (light gray) states. FTO/glass was used for the baseline (black).

### ASSOCIATED CONTENT

** Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c08087.

Experimental details, materials, and methods; crystal data and structure refinement for SolCON-B; NBED of SolCON-A; spectrophotometric and electrochemical characterization of SurCON; characterization of the network formed from PdCl$_2$(PhCN)$_2$ and iron complex 1 (PDF)

### Accession Codes

CCDC 2095187 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

### AUTHOR INFORMATION

** Corresponding Authors**

Michal Lahav — Department of Molecular Chemistry and Materials Science, The Weizmann Institute of Science,
ACKNOWLEDGMENTS

This research was supported by the Helen and Martin Kimmel Center for Molecular Design and the Israel Science Foundation (ISF). M.E.v.d.B. is the holder of the Bruce A. Pearman Professional Chair in Synthetic Organic Chemistry. We thank Dr. Tatyana Bendikov for XPS measurements, and Dr. Olga Brontvein and Dr. Ifat Kaplan-Ashiri for electron microscopy imaging.

REFERENCES

(1) Freund, R.; Canossa, S.; Cohen, S. M.; Yan, W.; Deng, H.; Guillerm, V.; Eddaoudi, M.; Madden, D. G.; Fairen-Jimenez, D.; Lyu, H.; Macrèdo, L. K.; Ji, Z.; Zhang, Y.; Wang, B.; Haase, F.; Woll, C.; Zaremba, O.; Andreo, J.; Wuttke, S.; Diercks, C. S. 25 Years of coordination cages based on banana-shaped ligands. Chem. Soc. Rev. 2014, 43, 1848–1860.

(10) Sarma, R. J.; Nitschke, J. R. Self-assembly in systems of subcomponents: simple rules, subtle consequences. Angew. Chem., Int. Ed. 2008, 47, 377–380.

(11) Furukawa, H.; Cordova, K. E.; O’Keeffe, M.; Yaghi, O. M. The chemistry and applications of metal-organic frameworks. Science 2013, 341, 1230444.

(12) Rieth, A. J.; Wright, A. M.; Dincă, M. Kinetic stability of metal-organic frameworks for corrosive and coordinating gas capture. Nat. Rev. Mater. 2019, 4, 708–725.

(13) Kobayashi, A.; Ohba, T.; Saitoh, E.; Suzuki, Y.; Noro, S.-I.; Chang, H.-C.; Kato, M. Flexible Coordination Polymers Composed of Luminescent Ruthenium(II) Metalloigands: Importance of the Position of the Coordination Site in Metalloigands. Inorg. Chem. 2014, 53, 2910–2921.

(14) Zhang, X.; Chen, Z.; Liu, X.; Hanna, S. L.; Wang, X.; Ledari, R. T.; Maleki, A.; Li, P.; Farha, O. K. A historical overview of the activation and porosity of metal-organic frameworks. Chem. Soc. Rev. 2020, 49, 7406–7427.

(15) Colwell, K. A.; Jackson, M. N.; Torres-Gavosto, R. M.; Jawahery, S.; Vlassiavlerich, B.; Falkowski, J. M.; Smit, B.; Weston, S. C.; Long, J. R. Buffered Coordination Modulation as a Means of Controlling Crystal Morphology and Molecular Diffusion in an Anisotropic Metal‐Organic Framework. J. Am. Chem. Soc. 2021, 143, 5044–5052.

(16) de Ruiter, G.; Lahav, M.; van der Boom, M. E. Pyridine Coordination Chemistry for Molecular Assemblies on Surfaces. Acc. Chem. Res. 2014, 47, 3407–3416.

(17) de Ruiter, G.; van der Boom, M. E. Surface-Conﬁned Assemblies and Polymers for Molecular Logic. Acc. Chem. Res. 2011, 44, 563–573.

(18) Wu, K.; Zhang, B.; Drechsler, C.; Holstein, J. J.; Clever, G. H. Backbone-Bridging Promotes Diversity in Heteroleptic Cages. Angew. Chem., Int. Ed. 2021, 60, 2–31.

(19) Carpenter, J. P.; McTernan, C. T.; Greenfield, J. L.; Lavendomme, R.; Ronson, T. K.; Nitschke, J. R. Controlling the Shape and Chirality of an Eight-crossing Molecular Knot. Chem. 2021, 17, 1534–1543.

(20) Mukherjee, S.; Mukherjee, P. S. Template-free multicomponent coordination-driven self-assembly of Pd(ii)/Pt(ii) molecular cages. Chem. Commun. 2014, 50, 2239–2248.

(21) Sun, Y.; Chen, C.; Liu, J.; Stang, P. J. Recent developments in the construction and applications of platinum-based metallocycles and metallacages via coordination. Chem. Soc. Rev. 2020, 49, 3889–3919.

(22) M. Kinetic stability of metal-organic frameworks. Nat. Commun. 2020, 11, 380.

(23) di Gregorio, M. C.; Shimon, L.; Brumfeld, V.; Lahav, M.; van der Boom, M. E. Unusual Surface Texture, Dimensions and Morphology Variations of Chiral and Single. Angew. Chem. Int. Ed. 2021, 60, 18256–18264.

(24) Mondal, S.; Chandra Santra, D.; Ninomiya, Y.; Yoshida, T.; Higuchi, M. Dual-Redox System of Metallo-Supramolecular Polymers for Visible-to-Near-IR Modulable Electrochromism and Durable Device Fabrication. ACS Appl. Mater. Interfaces 2020, 12, 58277–58286.

(25) Takada, K.; Sakamoto, R.; Yi, S.-T.; Katagiri, S.; Kambe, T.; Nishihara, H. Electrochromic Bis(terpyridine)metal Complex Nanosheets. J. Am. Chem. Soc. 2015, 137, 4681–4689.
(29) Mondal, P. C.; Singh, V.; Zharnikov, M. Nanometric Assembly of Functional Terpyridyl Complexes on Transparent and Conductive Oxide Substrates: Structure, Properties, and Applications. Acc. Chem. Res. 2017, 50, 2128–2138.

(30) Schott, M.; Szczepańska, W.; Kurth, D. G. Detailed Study of Layer-by-Layer Self-Assembled and Dip-Coated Electrochromic Thin Films Based on Metallo-Supramolecular Polymers. Langmuir 2014, 30, 10721−10727.

(31) Cui, B.; Tang, J.-H.; Yao, J.; Zhong, Y.-W. A Molecular Platform for Multistate Near-Infrared Electrochromism and Flip-Flop, Flip-Flap-Flop, and Ternary Memory. Angew. Chem., Int. Ed. 2015, 54, 9192–9197.

(32) Malik, N.; Lahav, M.; van der Boom, M. E. Electrochromic Metallo-Organic Nanoscale Films: A molecular Mix and Match Approach to Thermally Robust and Multistate Solid-State Devices. Adv. Electron. Mater. 2020, 6, 2000407.

(33) Laschuk, N. O.; Ahmad, R.; Ebralidze, I. I.; Poisson, J.; Easton, E. B.; Zhenkina, O. V. Multichromic Monolayer Terpyridine-Based Electrochromic Materials. ACS Appl. Mater. Interfaces 2020, 12, 41749–41757.

(34) Malik, N.; Eholoov, N.; de Ruiter, G.; Lahav, M.; van der Boom, M. E. On-Surface Self-Assembly of Stimuli-Responsive Metallo-Organic Films: Automated Ultrasonic Spray-Coating and Electrochromic Devices. ACS Appl. Mater. Interfaces 2019, 11, 22858–22868.

(35) Lahav, M.; van der Boom, M. E. Polypyrrolyl Metallo-Organic Assemblies for Electrochromic Applications. Adv. Mater. 2018, 30, 1706641.

(36) Beves, J. E.; Constable, E. C.; Housecroft, C. E.; Neuberger, M.; Schaffner, S. A one-dimensional copper(ii) coordination polymer containing $\text{Fe}([\text{pytpy}]_2)$: (pytpy = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine) as an expanded 4,4′-bipyridine ligand: a hydrogen-bonded network penetrated by rod-like polymers. CrystEngComm 2008, 10, 344–348.

(37) Gupta, T.; Mondal, P. C.; Kumar, A.; Jeyachandran, Y. L.; Zharnikov, M. Surface-Confinned Heterometallic Molecular Dyads: Merging the Optical and Electronic Properties of Fe, Ru, and Os Terpyridyl Complexes. Adv. Funct. Mater. 2013, 23, 4227–4235.

(38) Arslan, H. K.; Shekhaih, O.; Wohlgenoth, J.; Franzreb, M.; Fischer, R. A.; Woll, C. High-Throughput Fabrication of Uniform and Homogenous MOF Coatings. Adv. Funct. Mater. 2011, 21, 4228–4231.

(39) Chernikova, V.; Shekha, O.; Eddaaoudi, M. Advanced Fabrication Method for the Preparation of MOF Thin Films: Liquid-Phase Epitaxy Approach Meets Spin Coating Method. ACS Appl. Mater. Interfaces 2016, 8, 20459–20464.

(40) Wen, Q.; Tenenholtz, S.; Shimon, L. J. W.; Bar-Elli, O.; Beck, L. M.; Houben, L.; Cohen, S. R.; Feldman, Y.; Oron, D.; Lahav, M.; van der Boom, M. E. Chiral and SHG-Active Metal-Orgaic Frameworks Formed in Solution and on Surfaces: Uniformity, Morphology Control, Oriented Growth and Post-assembly Functionalization. J. Am. Chem. Soc. 2020, 142, 14210–14211.

(41) Fan, Q.; Luy, J.-N.; Liebhold, M.; Greulich, K.; Zugermeier, M.; Sundermeyer, J.; Tonner, R.; Gottfried, J. M. Template-controlled on-surface synthesis of a lanthanide supranaphthalocyanine and its open-chain polycyanine counterpart. Nat. Commun. 2019, 10, 5049.

(42) Schoedel, A.; Wojtas, L.; Kelley, S. P.; Rogers, R. D.; Eddaaoudi, M.; Zaworotko, M. J. Network Diversity through Decoration of Trigonal-Prismatic Nodes: Two-Step Crystal Engineering of Cationic Metal-Organic Materials. Angew. Chem., Int. Ed. 2011, 50, 11421–11424.

(43) Xu, H.-S.; Luo, Y.; See, P. Z.; Li, X.; Chen, Z.; Zhou, Y.; Zhao, X.; Lang, K.; Park, I.-H.; Li, R.; Liu, C.; Chen, F.; Xi, S.; Sun, J.; Lob, K. P. Divergent Chemistry Paths for 3D and 1D Metallo-Covalent Organic Frameworks (COFs). Angew. Chem., Int. Ed. 2020, 59, 11527–11532.

(44) Schäfer, B.; Greisch, J.-F.; Faus, I.; Bodenstein, T.; Šaltík, L.; Fuhr, O.; Fink, K.; Schünemann, V.; Kappes, M. M.; Ruben, M. Divergent Coordination Chemistry: Parallel Synthesis of $[2 \times 2]$