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Article

Emergence of Coordination-Mediated Electronic States in Disordered Ni-Polyphenyl Architectures

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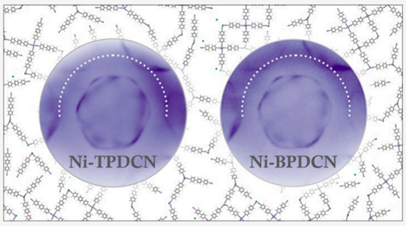

ABSTRACT: The on-surface coordination of transition metals with *π*-extended organic molecules offers a versatile strategy to tailor electronic states in low-dimensional systems. However, the relationship between structural order and coordination-mediated electronic properties remains underexplored. Here, we investigate the self-assembly of two nitrile-functionalized polyphenyl ligands, [1,1′:4′,1″-terphenyl]-4,4″-dicarbonitrile and biphenyl-4,4′-dicarbonitrile, on Ag(111), and examine the effects of subsequent Ni coordination. Low-energy electron diffraction confirms the formation of ordered self-assembled monolayers prior to metal coordination, while valence band spectroscopy indicates weak interaction with the Ag(111) substrate. Upon Ni coordination, the long-range order is disrupted, and new electronic states appear in the valence band region. Momentum-resolved photoemission reveals that these coordination-induced states exhibit weak dispersive character, consistent with metal−ligand orbital coupling and indicative of electronic delocalization. These findings demonstrate that coordination can induce robust electronic functionality even in structurally disordered two-dimensional metal−organic architectures.

INTRODUCTION

The principles of supramolecular chemistry represent a flexible approach for designing molecular interfaces, with applications in gas sensing, data storage, and molecular electronics.[1−4] A key challenge in this field is to understand how different intermolecular and interfacial interactions influence the structural and electronic properties of self-assembled systems.[5−7] While noncovalent forces such as van der Waals or dipolar interactions and hydrogen bonding govern molecular organization,[8] these interactions are often weak and do not significantly alter the electronic structure of the assembled systems.[9,10] In contrast, metal−ligand coordination introduces stronger interactions that not only stabilize molecular architectures, but also modulate their electronic properties, offering a rationale to tune interfacial behavior in organic-based structures.[11−13]

The on-surface coordination of transition metals (TMs) by *π*-extended organic ligands has emerged as a powerful strategy for engineering functional nanomaterials.[14−18] Among the diverse ligands explored in surface coordination chemistry, dicarbonitrile-polyphenyl molecular linkers are particularly attractive due to their electron-withdrawing nitrile (CN) groups. These functional groups facilitate metal−organic coordination-driven hybridization with the electronic states of TM atoms, leading to diverse supramolecular architectures with tunable electronic properties.[19,20] Scanning tunneling microscopy (STM)-based studies have demonstrated the remarkable versatility of these molecules in two-dimensional metal−organic frameworks (2D MOFs) formation, enabling the successful creation of nanoporous networks,[21−24] as well as fully interconnected 2D random coordination systems by tuning molecular coverage.[25]

Notably, as reported by Schlickum et al., surface molecular coverage plays a critical role in driving structural transitions.[26] When the molecular coverage exceeds that of the saturated monolayer nanomesh, the evaporation of Co atoms induces the formation of a metal−organic pattern with random coordination. These irregular patterns provide valuable insights into the nature of disordered materials through the identification of elementary structural motifs and defects. Similarly, complementary investigations have revealed that disordered coordination networks incorporating TM centers with nonlinear prochiral ditopic linkers form nodal coordination motifs of similar energy, resulting in bifurcation or string formation.[27] This energetic equivalence drives a divergent assembly scenario, ultimately resulting in random surface architectures.

Building on these findings, the study of disordered 2D metal−organic architectures has attracted increasing interest, particularly due to their real-world applications where long-range structural order is absent. This highlights the importance

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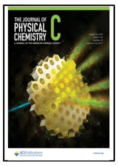

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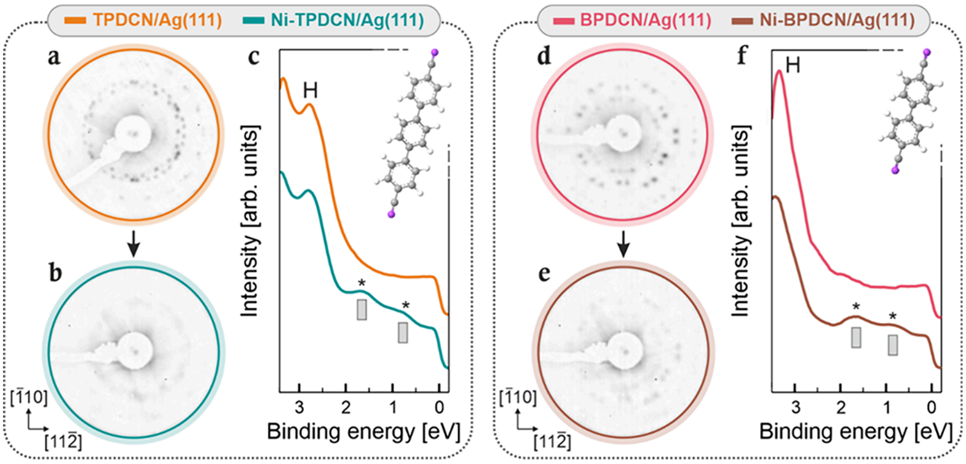

Figure 1. (a, b) LEED patterns of TPDCN/Ag(111) and Ni-TPDCN/Ag(111) systems, respectively, taken at the energy of 20 eV. (c) Experimental VB spectra (photon energy 30 eV, p-polarized light) acquired for the TPDCN/Ag(111) (orange curve) and Ni-TPDCN/Ag(111) (green curve). The structure model of TPDCN molecule is depicted above the VB spectra (gray, C; purple, N; white, H). (d, e) LEED patterns of BPDCN/Ag(111) and Ni-BPDCN/Ag(111) systems, respectively, taken at the energy of 20 eV. (f) Experimental VB spectra (photon energy 30 eV, p-polarized light) acquired for the BPDCN/Ag(111) (pink curve) and Ni-BPDCN/Ag(111) (brown curve). The structure model of BPDCN molecule is depicted above the VB spectra (gray, C; purple, N; white, H).

of treating structural and electronic design principles as distinct but interrelated aspects.[28−30]

Despite extensive structural characterizations of these systems, the influence of metal coordination and molecular design on coordination-mediated electronic states in partially ordered or disordered phases remains not fully understood. Further studies are needed to unveil the complex interplay between orbital interactions and structural irregularities.

To address this challenge, we investigate the self-assembly and Ni-induced modification of electronic states in two nitrile-functionalized molecules on Ag(111). Specifically, we compare the metal−ligand coordination behavior of [1,1’:4’,1’’-terphenyl]-4,4’’-dicarbonitrile (terphenyl-dinitrile, TPDCN) and biphenyl-4,4’-dicarbonitrile (biphenyl-dinitrile, BPDCN). This comparison enables evaluation of how the molecular flexibility influences metal−ligand interaction and orbital overlap in partially ordered phases. Our findings provide new insights into the role of coordination chemistry in tuning interfacial electronic properties, bridging the gap between structural disorder and functional electronic behavior in metal−organic systems.

The low energy electron diffraction (LEED) analysis confirms that both molecules, prior to metal coordination, form well-ordered, self-assembled monolayers on Ag(111), stabilized by substrate templating and intermolecular interactions, as evidenced by the presence of mirror domains reflecting the substrate symmetry. Valence band (VB) spectroscopy reveals that these layers interact weakly with the metal substrate, exhibiting no occupied lowest unoccupied molecular orbital (LUMO)-derived states near the Fermi level (E_F).[31] This suggests minimal interfacial charge transfer, allowing the molecules to retain their intrinsic electronic characters. Upon Ni coordination, however, the LEED patterns become diffuse and the diffraction spots’ intensity significantly weakens, indicating structural changes, transitioning to more disordered metal−organic phases. Complementary, the VB spectra exhibit new features at lower binding energies (BEs), consistent with the energy range of Ni 3d orbitals in Ni-ligand MOFs.

These changes demonstrate the emergence of new electronic states resulting from the metal−ligand interactions and orbital overlap between the Ni 3d orbitals and the ligand states, even in the absence of long-range structural order.

■ RESULTS AND DISCUSSION

The adsorption and self-assembly of terphenyl-dinitrile and biphenyl-dinitrile on Ag(111) have been first characterized using LEED (Figure 1a, d, respectively). Both molecules form well-ordered monolayers, as evidenced by sharp diffraction patterns, leading to commensurate superstructures. LEED simulations yield a superstructure matrix of (3:2/5:15) for terphenyl-dinitrile and (3:2/4:9) for biphenyl-dinitrile (Figure S1). These matrices correspond to periodic structures that are in registry with the underlying Ag(111) surface. Although rotation domains are observed, the long-range order is attributed to the substrate templating, wherein the Ag(111) surface symmetry manifests in the azimuthal alignment of molecules within local domains, promoting directional intermolecular interactions. However, due to the coexistence of multiple azimuthal orientations (rotational domains), not all molecules exhibit the same alignment across the surface. This behavior is consistent with prior studies of linear-based dicarbonitrile-polyphenyl systems, transitioning from chevron-like arrangements at low coverage to densely packed and parallel-aligned structures upon monolayer saturation.[22,25,32,33] Moreover, previous near-edge X-ray absorption fine structure (NEXAFS) and STM studies suggest that these molecules adopt a flat-lying adsorption geometry, with the molecular reference plane oriented parallel to the Ag(111) surface, consistently with the derived unit cell dimensions.[32]

To acquire additional insights beyond structural characterization, the analysis is extended to their electronic properties. VB spectra of the pristine Ag(111) substrate are dominated by its broad sp band, appearing featureless up to approximately 4.0 eV BE (Figure S3a, b). In contrast, the molecular layers display distinct peaks at ∼2.8 eV and ∼3.3 eV BE, which are assigned to the highest occupied molecular orbitals (HOMOs, marked with “H”) of the terphenyl- and biphenyl-dinitrile, respectively (Figure 1c, f). An additional feature at ∼3.4 eV in

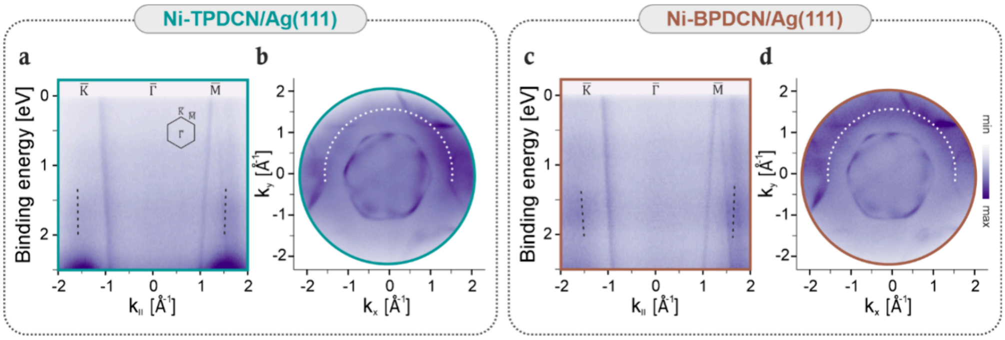

Figure 2. Momentum-resolved band maps along the high-symmetry direction $\bar{K} - \bar{\Gamma} - \bar{M}$ of the surface Brillouin zone of Ag(111) measured for: (a) Ni-TPDCN/Ag(111) and (c) Ni-BPDCN/Ag(111) systems, collected at a photon energy of 30 eV using p-polarized light (dashed lines as a visual guide to the band dispersion). Constant binding energy (~1.7 eV) momentum images of (b) Ni-TPDCN/Ag(111) and (d) Ni-BPDCN/Ag(111), collected at a photon energy of 30 eV using p-polarized light.

the spectra measured for the terphenyl-dinitrile layer corresponds to a deeper-lying occupied molecular state, reflecting the intrinsic electronic structure of the molecule. Importantly, no states are observed near the Fermi level (E_F), where the LUMO would appear if partially occupied.[14−16] In fact, in systems with significant molecule−substrate charge transfer, electron donation or hybridization often populates the LUMO, yielding a clear spectral signature.[18,34,35] In the present system, the absence of molecular-derived states near the Fermi level (binding energy range: 0.0−1.5 eV) in the VB spectra confirms that the interaction is weak and does not involve significant charge transfer, keeping the LUMOs unoccupied. This is consistent with the relatively low electron affinity of the terphenyl-dinitrile and biphenyl-dinitrile molecules, compared to other organic-based systems,[34,36] and their planar adsorption geometry, which limits orbital overlap with the substrate.

This weak interaction can be attributed to two synergistic factors. On the one hand, the relatively inert nature of Ag(111) minimizes charge transfer compared to more reactive metal interfaces. On the other hand, the weak bonding of the CN groups on Ag(111) preserves the integrity of the molecular π-system.[24,26] The preservation of the native electronic properties highlights a key role of the Ag(111) substrate as a structural director rather than an electronic perturbator. This is particularly advantageous for hybrid interfaces, where intrinsic molecular functionality must dominate, as in single-atom catalysts or molecular spintronic devices.[37−40]

Following the characterization of the pristine molecular layers, we have investigated the structural and electronic effects of Ni coordination on the self-assembled terphenyl- and biphenyl-dinitrile monolayers. Upon subsequent deposition of Ni atoms onto the ordered molecular adlayers, the LEED patterns lose sharpness (Figure 1b, e), suggesting a transition to partially disordered phases. Given that the LEED probe averages over a beam spot of ~500 μm in diameter, this loss of sharp diffraction features suggests that the disorder extends across mesoscopic length scales. The observed structural heterogeneity likely arises from the coexistence of multiple coordination arrangements between Ni centers and the molecular CN groups. As a result, a variety of metal−organic motifs are formed, as reported in similar systems,[27] disrupting the long-range order previously established in pristine self-assembled arrays. Specifically, the coordination motifs of Ni atoms with the nitrile-functionalized biphenyl and terphenyl ligands can be inferred from previous STM studies on analogous systems. These studies report the formation of 2-fold, 3-fold, and 4-fold coordination geometries, giving rise to linear chains,[41] honeycomb motifs,[21] and square-planar arrangements,[20] respectively. Among these, 3-fold coordination has often been identified as the dominant motif.[22,26] Schematic illustrations of the plausible Ni coordination geometries are shown in Figure S2. The irregularity observed in our network likely arises from the coexistence of different coordination motifs, resulting in multiple molecular orientations and local defects that disrupt the long-range periodicity.

Starting from these structural changes, VB spectroscopy reveals the emergence of new electronic states at ~1.7 eV and ~0.8 eV BE for the terphenyl-dinitrile-based network and at ~1.7 eV and ~0.9 eV BE for the biphenyl-dinitrile-based network, marked with "*" (Figure 1c, f, respectively). These states, which are absent in pristine molecular layers, emerge upon Ni coordination and appear at BEs consistent with Ni 3d orbitals in metal−ligand complexes. In fact, their energy position and spectral character closely resemble hybrid electronic states reported in previous studies of 2D MOFs, where similar features in the ~0.5−2.0 eV BE range were attributed to strong orbital overlap between out-of-plane Ni $3d_{xz}/3d_{yz}$ orbitals and π-symmetric ligand orbitals.[15,16] This interaction involves charge transfer from Ni to the ligand, partially occupying ligand-based states and forming bonding/antibonding features visible in the VB.[18,35] Notably, the length and rigidity of the dicarbonitrile-polyphenyl linker play a critical role in modulating the electronic properties of the system by tuning the energy alignment between molecular orbitals and metal states, thereby enabling the design of tailored functionalities.[22] Although the electronic differences between the terphenyl- and biphenyl-dinitrile derivatives are relatively subtle, the terphenyl-based system exhibits slightly larger energy shifts (~0.9 eV vs ~0.8 eV) and broader spectral features in the VB. These slight differences are likely attributable to the steric constraints imposed by the terphenyl's three-ring backbone, which favors a more planar absorption geometry on the surface.[32] Such a configuration facilitates improved orbital overlap with Ni centers and neighboring ligands, thereby enhancing the metal−ligand interaction.

The terphenyl-dinitrile system achieves significant electronic interaction through intrinsic π-extension, which bridges localized CN−Ni coordination-mediated states via metal−ligand orbital hybridization, even in partially disordered phases with multiple metal−organic motifs. This behavior is in line with previous works on polymerized porphyrins, where

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dispersive bands emerged in structurally disordered Ni-tetraphenylporphyrin (Ni-TPP) assemblies.[42,43] Both systems leverage extended π-electronic interaction and flat adsorption to sustain coherence across defects, though the CN−Ni bonding actively promotes orbital overlap that amplifies partial electronic delocalization while retaining defect irregularities.

Further investigation of the electronic hybridization induced by Ni coordination in terphenyl- and biphenyl-dinitrile monolayers was performed using momentum-resolved photoemission microscopy. Despite the structural disorder, momentum-resolved photoemission reveals dispersive electronic bands along the $\bar{K} - \bar{\Gamma} - \bar{M}$ direction of the Ag(111) substrate (Figure 2a, c). These bands, which are absent in both the pristine molecular layers and the clean Ag(111) surface (Figure S3), arise from the coordination-induced electronic states resulting from orbital overlap between Ni 3d orbitals and the frontier π-orbitals of the ligands. These features exhibit a weak but discernible dependence on the in-plane momentum (k_{II}), indicative of limited band dispersion. To quantify this effect, we analyzed the binding energy range from 1.3 to 2.0 eV, where spectral features are most pronounced (Figure S4). For the terphenyl-dinitrile-based MOF, the estimated in-plane momentum band dispersions are $\Delta k_{II}(\bar{K} - \bar{\Gamma})$ = 0.02 Å^{-1} and $\Delta k_{II}(\bar{M} - \bar{\Gamma})$ = 0.06 Å^{-1}. In the case of the biphenyl-dinitrile-based MOF, the respective values are $\Delta k_{II}(\bar{K} - \bar{\Gamma})$ = 0.10 Å^{-1} and $\Delta k_{II}(\bar{M} - \bar{\Gamma})$ = 0.05 Å^{-1}. While this dispersion is much weaker than that typically observed in crystalline materials with long-range order, it nonetheless suggests the formation of hybrid states arising from interactions between Ni 3d orbitals and the π-symmetric orbitals of the ligands. Additionally, the VB spectra reveal a continuous distribution of electronic states rather than sharp, localized molecular features. This continuous density of states supports the presence of delocalized electronic interactions within the coordination network, even though the overall structural order remains short-range. The coexistence of weak dispersion and broad spectral weight implies that the electronic coupling extends over locally ordered motifs but lacks coherence across the full surface.

This behavior is reminiscent of previous observations in disordered Ni-TPP-based coordination networks, where dispersive bands with free-electron-like characters were found despite the absence of long-range order.[44] These findings point to the emergence of coordination-induced hybrid states with partial delocalization, governed by local geometry and orbital overlap, rather than global symmetry.

The polarization dependence of these features, in which the signal is stronger under p-polarized light and weaker under s-polarized light, confirms the π-character of these states, consistent with delocalized electronic features in MOF systems.[44] Moreover, the flat-lying adsorption geometry of the ligand plays a crucial role in this hybridization mechanism. In this orientation, the π-orbitals are aligned perpendicular to the surface, enabling effective overlap between adjacent molecules and Ni centers. This spatial configuration maximizes coupling between the ligand states and the Ni 3d orbitals (e.g., $3d_{xz}/3d_{yz}$).[15,35] As demonstrated by the energy momentum images in Figure 2b, d collected at ∼1.7 eV BE using p-polarized light, both networks display ring-like features in the reciprocal space, signatures of coordination-induced electronic structure modifications. In particular, these arise from the presence of multiple azimuthal orientations of the metal−organic motifs with respect to the Ag(111) substrate lattice, leading to a distribution of similar electronic states across different rotational domains. These findings are further corroborated by comparison with the graphene system exhibiting multiple rotational domains.[45−47]

In the terphenyl- and biphenyl-dinitrile systems, the Ni coordination induces partial delocalization of the ligand's π-electrons, even in the absence of a fully conjugated π-backbone. This delocalization, resulting from metal−ligand interactions and orbital overlap, facilitates coherent charge transport. This mechanism is analogous to that observed in doped conjugated polymers, where π-electron delocalization persists despite morphological disorder.[48,49] Here, Ni-mediated charge transfers into the π-systems through orbital overlap, establishing an extended delocalization pathway and providing robust charge transport channels that differ from traditional MOFs, which rely on long-range lattice regularity for conductivity.

The robustness of coordination-mediated states in disordered phases challenges conventional assumptions that long-range order is essential for achieving functional electronic coupling.[16,35] Our results demonstrate that targeted orbital interactions can still dominate in irregular architectures, provided that the molecular design optimizes orbital overlap and charge transfer. This approach may enable defect-tolerant applications such as flexible electronics, single-atom catalysis, and disordered MOFs, where functionality may arise from local delocalization and orbital-level interaction, rather than relying solely on global lattice symmetry. By linking coordination chemistry with π-extension, our work offers a new perspective for designing quantum materials in which localized orbital interactions govern emergent properties.

■ CONCLUSIONS

In summary, we demonstrate that self-assembled monolayers of terphenyl- and biphenyl-dinitrile on Ag(111) interact weakly with the substrate. Upon coordination with Ni, new hybrid electronic states emerge in the valence band spectra, indicating coordination-driven interactions between Ni 3d orbitals and the π-states of the ligands. Although the coordination networks exhibit significant structural disorder, momentum-resolved photoemission and polarization-dependent measurements reveal weak but finite dispersion of these states. This observation suggests partial electronic coherence within locally ordered motifs. Notably, the planar adsorption geometry of the terphenyl-dinitrile ligand enhances orbital overlap and promotes electronic coupling across coordination motifs. In contrast, the greater conformational flexibility of the biphenyl-dinitrile reduces this effect.

■ METHODS

Sample Preparation. The Ag(111) single crystal was cleaned by argon ion (Ar^+) sputtering at room temperature, followed by annealing to 770 K. The sputtering was conducted at an energy of 1.5−2.0 keV.

Terphenyl-dinitrile and biphenyl-dinitrile molecules were evaporated from a Knudsen-type evaporator at 450 and 350 K, respectively, onto the Ag(111) substrate, which was kept at 300 K. The quality of the self-assembled well-ordered monolayers was checked by SPECS LEED (spot size of ∼500 μm).

Nickel was evaporated from an e-beam evaporator operating at ion fluxes of 10 nA onto the TPDCN/Ag(111) and BPDCN/Ag(111) interfaces, which were kept at 300 K. After the deposition of Ni metal, both LEED patterns lost sharpness, indicating structural changes.

Photoemission Measurements. The photoemission experiments were conducted at the NanoESCA beamline of the synchrotron light source Elettra in Trieste, Italy, using a photoelectron emission microscope (PEEM).[50,51]

VB spectra were collected at a photon energy of 30 eV with linearly polarized light. All measurements were performed at a base pressure below 1×10^{-10} mbar, with the sample temperature maintained at 90 K. The total energy resolution, accounting for both the analyzer and beamline contributions, was 100 meV, while the momentum resolution of the PEEM was $\pm$ 0.05 Å^{-1}. To prevent photon beam-induced damage and ensure the acquisition of high-quality data, the samples were rastered during the experiment with a photon beam size of ~50 μm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.5c03063.

> Experimental LEED patterns and their simulations; schematic representation of the different coordination geometries between the Ni center and the coordinating molecules; constant binding energy momentum image of Ag(111) and momentum-resolved band maps for Ag(111), TPDCN/Ag(111) and BPDCN/Ag(111) systems; momentum-resolved band map for Ni-BPDCN/Ag(111) system and corresponding energy momentum line profiles (PDF)

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Author Contributions

Y.Y.G.Q. and V.F. performed the experiments and drafted the manuscript. S.M. contributed to the valence band experiments. All authors actively participated in the discussion of the results and the revision of the manuscript.

Notes

The authors declare no competing financial interest.

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