Toward Bioelectronic Nanomaterials: Photoconductivity in Protein–Porphyrin Hybrids Wrapped around SWCNT

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The development of sophisticated ordered functional materials is one of the important challenges in current science. One of the keys to enhance the properties of these materials is the control of the organization and morphology at different scales. This work presents a novel bioinspired methodology to achieve highly ordered donor/acceptor bio-nanohybrids using a designed repeat protein as scaffold, endowed with photoactive and electron donating porphyrin (P) units, to efficiently wrap around electron accepting single wall carbon nanotubes (SWCNT). A systematic experimental and theoretical study to evaluate the effect of the length of the protein reveals that longer proteins wrap around the SWCNT in a more efficient manner due to the stronger supramolecular interaction existing between the inner concave surface of the protein (namely Trp and His residues) and the convex surface of the (7,6)-SWCNT. Interestingly, spectroscopy and X-ray diffraction data further confirm that the so-called protein-P–SWCNT donor–acceptor bio-nanohybrids retain the original protein structure. Finally, the new bio-nanohybrids show a remarkable enhancement on the photoconductivity values by flash-photolysis microwave conductivity (FP-TRMC technique) demonstrating that the major charge carriers of electrons are injected into the SWCNTs and move along the 1D-structures.

1. Introduction

Symbiosis between carbon nanotubes (CNTs) and biological entities to create nanohybrid materials is a cutting-edge area with high impact in fields such as biomedicine, sensing, and energy production, just to name a few.[1] Up to now, DNA–CNT bio-nanohybrids are leading this research area due to the well-established and accurate design and manufacture of artificial nucleic-acid structures.[2] By contrast, the use of proteins for the generation of protein–CNT hybrids for optoelectronic applications is not so expanded presumably on behalf of the gap between the development of protein design comparing with that of DNA nanotechnology. However, in the last years, both computational and experimental studies have demonstrated the great potential of proteins and oligopeptides as biological frameworks for the functionalization and organization of CNTs. The main reason that makes proteins a powerful tool for nanotechnological applications is the extended number of building blocks comparing with DNA, with 20 different proteogenic amino acids considering only the canonical ones, with the concomitant possibility to tune more precisely the final properties of the so-called biological materials.[3]

Rationally, a requirement of these biological nanohybrids for being applied in light-harvesting and electron transfer devices is the introduction of an appropriate electron donor entity, acting the CNT as the electron acceptor material. In this line, a singular example presented by D’Souza et al. can be found in literature in which a three-component hybrid, porphyrin–DNA–CNT, is utilized for photoinduced electron transfer processes.[4] However, to the
best of our knowledge, donor–protein–CNT hybrids remain still unexplored.

In a previous work, we presented a novel bioinspired approach in which photoactive porphyrin derivatives were covalently connected to the helical scaffold of a designed repeat protein, in particular a consensus tetratricopeptide repeat (CTPR) protein, giving rise to an ordered and oriented bioorganic conjugate.\cite{5} Specifically, a mutated CTPR protein with four repeated units was designed, introducing two cysteine residues in each repeat to provide unique reactivity for the immobilization of the porphyrin derivatives. The hybrid conjugates retained the structure and assembly properties of the protein scaffold and displayed the spectroscopic features of orderly aggregated porphyrins along the protein structure.\cite{5} Herein, we present the creation of novel protein–SWCNT donor–acceptor bio-nano-hybrids from our recent bioinspired approach with potential applications in the so-called “biomolecular electronics.”

2. Results and Discussion

2.1. Compatibility of Morphology and Composition of CTPR Proteins and SWCNTs

The TPR motif consists of 2–20 tandem-repeats of 34 amino acids residues adopting a helix–turn–helix arrangement.\cite{6} Because of their modular nature repeat proteins are well suited to be used as biomolecular scaffolds.\cite{7} These CTPR repeats generate a right-handed superhelical structure\cite{8} producing two protein surfaces: an inner concave face which contributes mainly to ligand recognition in natural domains and a solvent exposed outer convex face.\cite{8b} Thus, the concave face presents two protein surfaces: an inner concave face which contributes mainly to ligand recognition in natural domains and a solvent exposed outer convex face.\cite{8b} Thus, the concave face presents an attractive frame for the accommodation of the hydrophobic SWCNT surface (Figure 1a).

Favorable binding between protein residues and CNT surface is mandatory for an effective interaction. In this sense, a deep search in literature of the reported noncovalent forces ruling the adsorption of peptides and proteins onto CNT surfaces was made. This examination was aimed to validate the composition of the protein and, if possible, to modify those nonconserved positions of the repeat sequence by more interacting amino acids residues adopting a helix–turn–helix arrangement.\cite{6} Considering this fact, and the understanding of the π–π(X = C, N) contacts,\cite{3,e,9} In this sense, Trp, Tyr, Phe, and His are good candidates to be localized in those positions forming part of the concave face in CTPR proteins. Among these, important experimental evidences demonstrated that peptide sequences rich in Trp and His show strong interactions with the CNT surface.\cite{11,10}

As described in recent theoretical and experimental works, the strongest interacting residues with CNTs are those bearing aromatic units in their side chain repeats by establishing π–π and XH···π(X = C, N) contacts.\cite{3,e,9} In this sense, Trp, Tyr, Phe, and His are good candidates to be localized in those positions forming part of the concave face in CTPR proteins. Among these, important experimental evidences demonstrated that peptide sequences rich in Trp and His show strong interactions with the CNT surface.\cite{11,10}

As previously described, surface exposed residues on the concave face in TPR proteins are mainly localized in helix A (Figure 2a), and usually encode specific binding to target guests.\cite{13} Considering this fact, and the understanding of the consensus positions in TPR sequence, positions 5 and 9, both localized on the concave protein surface, were modified by His residues to increase the interaction with the CNT wall. Luckily, Tyr residues are found in the original sequence of CTPR unit, two of them with the phenol group pointing through the concave face. Altogether, two His and two Tyr in each repeat fragment could play a major role in the favorable interaction of the protein with the CNT (Figure 1b).

2.2. Design and Synthesis of CTPR Proteins and Conjugates

For the study described herein, we employ three mutated TPR proteins with different numbers of CTPR repeats (CTPR4, CTPR8, and CTPR16) and their corresponding conjugates (CTPR4-P, CTPR8-P, and CTPR16-P) with our previously described zinc–metalloporphyrin P, bearing ethenylene glycol chains to ensure water solubility and a cysteine-reactive maleimide group for the conjugation with the protein (see the Supporting Information for further description of P). The previously described mutated CTPR4 was used as the smallest protein scaffold, with a dimension of ≈40 × 36 Å and eight cysteine residues in the outer area of the superhelix, in particular, in the four loops of the protein, for the conjugation with the maleimide-type porphyrin P. The distance between the Cys side chains is 7 and 8 Å, in the order of the distance required to establish π–π interactions between the porphyrin rings. Meanwhile, two new mutated proteins were designed, that is, CTPR8 and CTPR16. CTPR8 consisted on eight repeat units comprising one superhelical turn with overall molecular dimensions of ≈80 × 36 Å and 16 cysteine residues. Finally, CTPR16, with two superhelical turns, a dimension of 160 × 36 Å and 32 cysteine residues, was the largest biological framework. Moreover, two His residues per repeat unit were introduced in

![Figure 1. Suitability of morphology and composition of CTPR proteins with SWCNTs. a) Model of a CTPR8 (PDB ID: 2AVP\textsuperscript{10b}) and a (7,6)-SWCNT showing the morphological compatibility between the concave face of the protein and the SWCNT surface. b) Axial view along the superhelical axis of a CTPR8 highlighting the Tyr residues (red) and the engineered His residues (green).](image-url)
the sequence of the proteins (Figure 2a). As expected, the two Cys and two His mutations in each repeat unit did not significantly affect the helical structure of the protein scaffold. Thus, well-expressed, stable protein samples with the same α-helical structure as the parent protein were obtained (Figure 2b,c).

The designed proteins and metalloporphyrin P were conjugated using the maleimide–cysteine chemistry and the analysis of the samples by gel electrophoresis showed that conjugates of higher molecular weight than their corresponding CTPR proteins were obtained. Specifically, conjugates presented more than double weight comparing with their unfunctionalized proteins, meaning a near quantitative yield in the conjugation reaction of the cysteine residues. When the gel was imaged without staining, the porphyrin fluorescence signal could be detected only in the lanes containing conjugates holding the porphyrin moieties, as expected (Figure S1, Supporting Information).

The purification of the protein–porphyrin conjugates from the excess of free porphyrin is a mandatory step to produce homogenous hybrid structures. It was successfully carried out using size exclusion chromatography with the same conditions previously reported for the purification of the CTPR4–porphyrin conjugates.\(^5\) As predicted, the elution time decreased while increasing the size of the conjugate (Figure S1, Supporting Information).

A precise quantification of the number of porphyrins attached to each protein was not possible to elucidate by mass spectrometry due to the high content in porphyrin molecules and the high molecular weight of these conjugates (80–87 kDa for CTPR8-P with 14–16 porphyrins and 158–171 kDa for CTPR16-P with 28–32 porphyrins), which probably made difficult the volatilization of the samples. The effectiveness of the conjugation reaction was qualitatively demonstrated using absorption spectroscopy by the relative intensity of the Soret absorption band of porphyrin P, at 430 nm, compared to the protein absorption band, at 280 nm. Figure 3a shows, on one hand, that the Soret and the Q-bands in the CTPR8-P and CTPR16-P conjugates were not displaced to neither higher or lower wavelengths comparing to the previously reported UV–vis spectrum of CTPR4-P, thus, the location of the porphyrins and their electronic communication should be comparable, that is, establishing J-type aggregates. On the other hand, the ratio of the absorbance at λ = 430 nm respecting to λ = 280 nm in the three conjugates unambiguously proved that the relative amount of porphyrins is maintained while the dimension of the protein is enlarged. In our previous work, we demonstrated by mass spectrometry that 6 to 8 porphyrins on average were attached to the CTPR4. Therefore, we can conclude that the effectiveness of the conjugation reaction is maintained in all the cases and is unaffected by the size increment in CTPR8-12 to 16 porphyrins, and CTPR16-24 to 32 porphyrins (Figure 3b).

Regarding secondary structure of the protein scaffold within the conjugate and the spatial organization of the porphyrin moieties, circular dichroism (CD) studies were carried out. In the absorption region of proteins, that is, from 260 to 190 nm, all conjugates revealed the feature CD signal for α-helical secondary structure presented in CTPR proteins (Figure 3c; Figure S2, Supporting Information). Furthermore, optical activity is exhibited in the Soret absorption band of achiral porphyrins, indicating a chiral arrangement of these chromophores within the conjugates (Figure 3d; Figure S2, Supporting Information). These results confirmed the ability of all the mutated CTPR proteins employed in this work to act as robust biological scaffolds for ordering organic chromophores.

### 2.3. Wrapping SWCNT by CTPR Proteins and Conjugates

After obtaining and characterizing the corresponding CTPR proteins and protein–porphyrin conjugates, they were evaluated as wrapping agents for SWCNTs. Both of them formed water-soluble hybrid assemblies with SWNTs, producing aqueous solutions that were stable for months in the fridge (see Figure S3 in the Supporting Information for complete description of the preparation of the nanohybrids).

Insights into protein–SWCNT and conjugate–SWCNT ground-state electronic interactions came from UV–vis spectroscopic experiments. The study performed on the protein–SWCNT nanohybrids is depicted in Figure 4a. Although only three lengths of CTPR proteins have been used for this study, some trends can be pointed out: at the same amount of protein, that is 0.005% (w/v), the larger systems were able to dissolve more effectively SWCNTs in aqueous media. In particular, CTPR16, with two completed superhelical turns, was the most efficient wrapping agent followed by CTPR8, with one superhelical turn. CTPR4, being the shortest biological scaffold, was also the least effective. All-atom molecular dynamics (MD) simulations of the CTPR4-16 in the presence of a 20 nm long (7,6)-SWCNT were performed to rationalize their different binding capacity, and provide an atomistic description of the recognition process (Figure 5). For each system, three replicas of 100 ns unbiased MD simulations were initially run followed by 100 ns of accelerated molecular dynamics (aMD) to enhance conformational sampling (see the Supporting Information for...
complete computational details). In the 200 ns (a)MD simulations, all CTPR4-16 systems gradually adopt a more extended conformation over the SWCNT surface, as observed in Figure 5 and in the increase of the standard deviation of the radius of gyration. The latter ranges from \( \approx 18.2 \pm 1.7 \), \( 29.0 \pm 2.1 \), and \( 47.9 \pm 3.0 \) Å for CTPR4-16, respectively. The more extended CTPR4-16 conformations maximize the \( \pi-\pi \) interactions of His, Tyr, and Trp residues located in the concave face of the protein with the SWCNT. The access to these extended conformations is in agreement with the previously reported flexibility of the CTPR superhelices.\(^{[12]}\) CTPR16 and CTPR8 systems can completely wrap the SWCNT. CTPR4 is less effective due to its shorter length that only covers half of the SWCNT perimeter. This is reflected in the binding affinities: CTPR16 exhibits by far the most favorable binding (\(-638.8 \pm 15.5 \) kcal\( \cdot \)mol\(^{-1}\)), followed by CTPR8 (\(-334.7 \pm 40.6 \) kcal\( \cdot \)mol\(^{-1}\)), and CTPR4 (\(-288.4 \pm 18.5 \) kcal\( \cdot \)mol\(^{-1}\)). Along the course of the simulations more favorable binding energies are obtained as the elongation of the protein chain enhances their interaction with the SWCNT (Figure 5).

The same comparative study was performed on the respective three conjugates. In order to establish the influence on the exfoliation and supramolecular functionalization of SWCNTs with the zinc–metalloporphyrin fragment P in the conjugates, a control experiment was carried out using the nonconjugated porphyrin P (see the Supporting Information for complete description). Figure S4 (Supporting Information) shows that more than 90% of the porphyrin is precipitated in the presence of SWCNT in aqueous medium.

UV–vis studies performed on the conjugates with SWCNTs are illustrated in Figure 4c with comparable results relating to their analogue nonconjugated proteins. The trend was similar to that in the proteins, that is, at the same amount of the conjugates, longer scaffolds were more effective wrapping agents for the carbon nanostructures. To rationalize the effect of porphyrin moieties on the binding affinities of the protein scaffolds with the SWCNT, MD simulations were performed on the smallest CTPR4-P/SWCNT conjugate (see Figure 5 and the Supporting Information for computational details). The binding energies are substantially enhanced by the inclusion of porphyrins (\(-288.4 \pm 18.3 \) and \(-586.8 \pm 17.1 \) kcal\( \cdot \)mol\(^{-1}\) for CTPR4 and CTPR4-P, respectively). As shown in Figure 5, the increase in the binding affinity mainly comes from the interaction of the porphyrin moieties with the surface of the SWCNT, which completely wrap the nanotube perimeter by the end of the MD simulation. These results are in concordance with the effect
observed in the visible range of the Soret band of the zinc–metalloporphyrins that decreased, in spite of the increasing intensities in the whole spectral region of protein–SWCNT (Figure 4c).

Structural integrity of the proteins and conjugates, when they constitute their corresponding nanohybrids with SWCNTs, was proven by CD assays. Figure 4b,d and Figure S5 (Supporting Information) show how the $\alpha$-helix signature of CTPR framework is maintained in all the cases. The only difference to point out is the slight reduction in the dichroic signal comparing with the pristine samples without SWCNTs. This experimental finding could be attributed to a decrease of the protein/conjugate concentration during the centrifugation process. CNTs without a dense covering of proteinaceous material could precipitate out of the aqueous solution, carrying with them some wrapped macromolecules. Nevertheless, partial unfolding of the $\alpha$-helices could be another explanation to take into account.

Once identified CTPR16 protein and its corresponding CTPR16-P conjugate as the best dissolving agents of SWCNTs, the following assays are described only for their resultant nanohybrids: concomitant studies came from Raman spectroscopy which provided valuable information regarding the interaction between both entities. The first evidence to note is that D band intensity, relating to G bands, reveals no difference comparing with pristine SWCNTs, as expected from a noncovalent interaction (Figure 6a). By contrast, G-modes, shown in Figure 6b, reveal a downshifted from 1592 cm$^{-1}$ in pristine SWCNTs, to 1589 and 1585 cm$^{-1}$ in CTPR16/CNT and CTPR16-P/CNT, respectively. Previous studies have demonstrated that the G band peak in CNTs shifts to lower frequencies when doping with electron donor agents and to higher frequencies with electron acceptor ones.[13] However, in a reported work using peptides as wrapping agents of SWCNTs, even with modified Phe residues by Tyr residues (more electron donor moieties), the G-mode is upshifted comparing with uncoated SWCNTs. Only when comparing a Phe-rich peptide/CNT with a Tyr-rich peptide/CNT, a slight downshift of the G-mode was appreciated (0.6 cm$^{-1}$).[10a] However, in our current case, a remarkable downshift of 3 cm$^{-1}$ in CTPR16/CNT comparing with pristine SWCNT was found (Figure 6b). This experimental finding attested the strong interactions of electron-donating residues in CTPR16 with the surface of the nanotube. In particular, the 32 His and 32 Tyr presented in the concave face of CTPR16 could be responsible of such substantial shift to lower frequencies in the G band peak of SWCNTs. In the case of CTPR16-P conjugate, the effect was even more pronounced, with a downshift of 7 cm$^{-1}$, supplying evidence of a possible charge transfer process between the porphyrins and the SWCNTs (Figure 6b).

Transmission electron microscopy (TEM) provided conclusive support of the existence of the protein–CNT and conjugate–CNT nanohybrids. TEM images were acquired by drop-casting the

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**Figure 4.** Spectroscopic characterization of the bio-nanohybrids and the bioorganic nanohybrids. a) UV–vis spectra of CTPR4 (yellow line) (similar spectra were obtained for CTPR8 and CTPR16), CTPR4/CNT (grey dashed line), CTPR8/CNT (grey solid line), and CTPR16/CNT (black solid line). b) CD spectrum of CTPR16/CNT. c) UV–vis spectra of CTPR4-P (purple line), CTPR4-P/CNT (grey dashed line), CTPR8-P/CNT (grey solid line), and CTPR16-P/CNT (black solid line). d) CD spectrum of CTPR16-P/CNT.
Figure 5. Representation of the evolution of the radius of gyration (in Å) of CTPR16 (in orange), CTPR8 (violet), CTPR4 (cyan), and the porphyrin conjugate CTPR4-P (red) along the 200 ns (a)MD simulations. The computed binding energies (in kcal·mol⁻¹) are represented every 50 ns of simulation for all systems. In the case of CTPR16 and CTPR4-P some representative snapshots are also displayed.

Figure 6. Raman spectroscopy and TEM images of the bioorganic nanohybrids. a) Normalized Raman spectra from 50 to 3000 cm⁻¹. b) Normalized Raman spectra in the region of G-mode. All of them have been acquired at an excitation wavelength of 785 nm. Pristine SWCNTs (black line), CTPR16/CNT (yellow line), CTPR16-P/CNT (purple line). c) TEM image of CTPR16/CNT nanohybrids. d) TEM image of CTPR16-P/CNT nanohybrids.
corresponding aqueous solution onto a carbon grid. Figure 6c,d and Figure S6 (Supporting Information) show that the nanotubes are in an excellent exfoliated state and most of the individual SWCNTs showed their walls covered by organic material, that is, the protein or the conjugate depending on the sample.

In our previous work, we described that these porphyrin–protein conjugates preserve their structural integrity in the solid state, when forming thin films.[5] Now, we produced the aforementioned thin films with these new hybrid materials and tested their features by X-ray diffraction (XRD). XRD data of the mutated CTPR16, its conjugate CTPR16-P, and their corresponding nanohybrids CTPR16/CNT and CTPR16-P/CNT all revealed a most intense broad signal at 2θ around 19°–21° (Figure S7, Supporting Information). This value with a d-spacing of around 0.43 nm has been previously associated to the α-helical pitch of tandem repeats configuring the superhelix.[14] Therefore, CTPR16 scaffold retained its superhelical conformation both with the enormous amount of porphyrins covalently attached to the structure and, more challenging, the interacting SWCNTs provided a transient with prompt rise and moderate decay features. Namely, water-processable CTPR16/CNT films retain the conductivity of CNTs. We disclosed that CTPR16-P/CNT displayed a conductivity transient whose profile was almost identical to that of CTPR16/CNT, indicating that the major charge carriers of electrons were injected into CNTs and mobile along the 1D-structures. The photocurrent transients within ~10 μs (Figure S9, Supporting Information) obey almost 2nd order recombination kinetics, suggesting local diffusion of electrons on CNT controls the recombination of positive/negative charge carriers. Presence of Zn porphyrin chromophores resulted in the effective charge carrier availability of excitation light over wide wavelength ranges. For example, photoexcitation of CTPR16-P/CNT by 420 nm laser pulses also exhibited photoconductive nature. This observation suggested that Zn porphyrins absorbed visible light and mobile charge carriers were generated on CNTs. Thus, nanohybrids of CTPR16-P/CNT revealed their excellent conductivity, photoabsorption capability, as well as water-based film processability.

2.4. Charge Carrier Transporting Properties of the Bio-Nanoconjugates

The present soluble nanohybrids accommodating conducting SWCNT and photoactive porphyrin systems are interesting for soft electronics or bioelectronics fields. The photocarrier injection and intrinsic charge carrier transporting properties were investigated by flash-photolysis microwave conductivity (FP-TRMC) technique that enables the device-less, noncontact evaluation of transient conductivity upon photogenerated charge carriers in CTPR16-P, CTPR16/CNT, and CTPR16-P/CNT with minimized damage of the scaffold structures.[13] Similarly to the previous demonstration for CTPR4-P,[5] a thin film of CTPR16-P showed a clear conductivity transient upon photoexcitation with 355 nm laser pulse (Figure 7) with long-lived stable charge carrier species, suggesting significant contribution from the local motion of positive charge carriers on P-arrays. Transient absorption spectra support the formation of photooxidized states on the P-arrays (Figure S8, Supporting Information), and the calculated yield of radical cations is $\phi = 4.0 \times 10^{-2}$, leading to the local mobility of holes on P-arrays as $\mu = 4.5 \times 10^{-3}$ cm² V⁻¹ s⁻¹. A dropcast film of CTPR16/CNT provided a transient with prompt rise and moderate decay features. Namely, water-processable CTPR16/CNT films retain the conductivity of CNTs. We disclosed that CTPR16-P/CNT displayed a conductivity transient whose profile was almost identical to that of CTPR16/CNT, indicating that the major charge carriers of electrons were injected into CNTs and mobile along the 1D-structures. The photocurrent transients within ~10 μs (Figure S9, Supporting Information) obey almost 2nd order recombination kinetics, suggesting local diffusion of electrons on CNT controls the recombination of positive/negative charge carriers. Presence of Zn porphyrin chromophores resulted in the effective charge carrier availability of excitation light over wide wavelength ranges. For example, photoexcitation of CTPR16-P/CNT by 420 nm laser pulses also exhibited photoconductive nature. This observation suggested that Zn porphyrins absorbed visible light and mobile charge carriers were generated on CNTs. Thus, nanohybrids of CTPR16-P/CNT revealed their excellent conductivity, photoabsorption capability, as well as water-based film processability.

3. Conclusions

In summary, we described a novel approach to achieve biomolecular electronic materials using a chemically modified protein as wrapping agent for SWCNTs. The optimal superhelical conformation of CTPR proteins and the possibility to mutate some residues to amino acids with potential larger interaction energies make them a good candidate to reach this goal. In this regard, we have demonstrated the effectiveness of our approach by a wide range of techniques, corroborating the introduction of the SWCNT into the inner cavity of the protein superhelix and the stability of the folding state of the protein even with the carbon nanostructure inside. Additionally, we have performed a comparative study considering the length of the protein, using CTPR4, CTPR8, and CTPR16, which reveals that the increase in the protein length improves the wrapping capability and thereby the binding affinity for SWCNT.

Moreover, this approach has been expanded to the conjugates with photoactive and redoxactive metalloporphyrins to obtain unprecedented biomolecular electronic nanohybrids, namely donor–acceptor protein-P–SWCNT. The ability of the protein–porphyrin conjugates for wrapping around...
(7,6)-SWCNTs has been demonstrated to be virtually identical than their corresponding nonconjugated proteins. However, it is important to remark two important features in these nanohybrids: (i) the increase in the binding affinity due to the favorable interaction of the porphyrin moieties with the surface of the SWCNTs; and (ii) a remarkable higher value of photoconductivity for these donor/acceptor bio-nanohybrids. Altogether, this bioinspired methodology paves the way to the use of repeat proteins as highly efficient, robust, and chemically versatile scaffolds to obtain highly ordered and unprecedented functional materials.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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