

Multiple Anion-Coordinated Assemblies Based on a C_2 -Symmetric Stilbene-Hydrazone- Urea Ligand: Structural Transformations, Guest Encapsulation, and Photo-Responsive Behavior

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Abstract

The rational integration of multiple functional motifs into a single ligand scaffold represents a powerful strategy for constructing stimuli-responsive supramolecular systems. Herein, we report a C_2 -symmetric multifunctional ligand (L) that incorporates anion-binding urea groups, a dynamic acylhydrazone linkage, and a photoswitchable trans-stilbene unit within a single molecular framework. Anion-directed self-assembly of L produces discrete triple-helical architectures with tetrahedral anions (SO_4^{2-} , PO_4^{3-}) or a pentagonal macrocyclic assembly with trigonal planar CO_3^{2-} , as unambiguously established by ^1H NMR spectroscopy and high-resolution electrospray ionization mass spectrometry (HR-ESI-MS). UV-Vis binding studies reveal that anion affinity follows the order $PO_4^{3-} > SO_4^{2-} > CO_3^{2-}$, providing a thermodynamic basis for anion-exchange-driven structural interconversion between assemblies. The differential encapsulation behavior of the sulfate triple helix toward betaine enables phosphate-triggered guest release, demonstrating a prototype chemical-stimulus-responsive delivery system. Orthogonally, irradiation at 365 nm induces concurrent E/Z isomerization of both the C = C and C = N bonds, as confirmed by characteristic NMR shifts and density functional theory (DFT) calculations, leading to complete disassembly of all complexes into mononuclear ligand–anion adducts. This dual-responsive platform, governed by independent chemical and photochemical stimuli, provides a versatile blueprint for the design of smart materials in sensing and controlled release applications.

1. Introduction

Supramolecular chemistry, broadly defined as the chemistry of non-covalent interactions, has evolved from fundamental studies of molecular recognition into a mature discipline capable of delivering functional materials for catalysis, sensing, drug delivery, and information storage^{1–2}. Within this field, the directed self-assembly of discrete architectures from well-defined building blocks has been particularly influential. Metal–ligand coordination chemistry has provided the conceptual and practical foundation for this enterprise: the geometrically precise and thermodynamically controllable nature of metal–ligand bonds has enabled the construction of metallocycles, cages, and extended metal–organic frameworks (MOFs) with remarkable structural diversity and functional versatility^{3–9}. Seminal contributions include the coordination-driven self-assembly of discrete metallacycles and cages^{3–6}, the development of host–guest nanovessels for catalysis and encapsulation⁷, and the reticular synthesis of permanently porous MOFs^{8–9}.

Building on these foundations, anion-coordination-driven self-assembly has emerged as a complementary and increasingly vibrant field^{10–11}. Anions are ubiquitous in chemistry and biology, playing crucial roles in enzymatic catalysis, signal transduction, and membrane transport; yet their use as templates for the construction of ordered supramolecular architectures presents distinct challenges relative to metal-directed assembly. Anions typically exhibit lower charge density, higher hydration energies, and more diffuse electron clouds than metal cations, making their selective recognition more demanding¹². Nevertheless, elegant receptor designs incorporating strong hydrogen-bond donors—

most notably urea, thiourea, and squaramide groups—have demonstrated high binding selectivity toward specific anions ^{13–14}. Pioneering work from Bowman-James ¹⁵, Custelcean ^{16–18}, and others has demonstrated that anion coordination through hydrogen bonding can template the formation of discrete helicates, grids, tetrahedra, and cage architectures with well-defined geometries that respond dynamically to chemical stimuli ¹⁹.

A particularly powerful design strategy is the incorporation of dynamic and photo-responsive elements directly into the anion-binding ligand scaffold ^{20–22}. The acylhydrazone linkage ($-\text{C}(=\text{O})-\text{NH}-\text{N}=\text{CH}-$) is especially attractive in this regard for several reasons. First, it serves as a reversible dynamic covalent bond that undergoes error-correcting exchange under mild acidic conditions, allowing thermodynamic self-sorting during assembly ²³. Second, it provides an additional $\text{C}=\text{N}$ double bond capable of E/Z isomerization, introducing a photochemically addressable switching element ^{24–25}. Third, the imine $\text{C}-\text{H}$ and adjacent amide $\text{N}-\text{H}$ protons contribute auxiliary hydrogen-bond-donor sites that work synergistically with urea groups to enhance anion-binding affinity and directionality. The integration of a stilbene unit further provides a second, orthogonal photoswitchable $\text{C}=\text{C}$ bond, enabling multi-stage photo-control over molecular geometry. Crucially, the geometric changes associated with E-to-Z isomerization of either or both bonds alter the spatial orientation of the urea binding vectors and the dimensions of the anion-binding cavity, providing a mechanism for light-triggered disruption of supramolecular assemblies. Compared to simple hydrazones, the acylhydrazone motif retains dynamic covalent exchange under mild conditions while exhibiting superior hydrolytic stability, affording adaptive error-correction without compromising architectural integrity ²⁶.

Herein, we report the design, synthesis, and comprehensive characterization of a novel C_2 -symmetric ligand **L** incorporating a central trans-stilbene backbone, two acylhydrazone linkages, and two terminal urea groups bearing nitrophenyl substituents. Through systematic variation of the templating anion, **L** forms three structurally distinct supramolecular assemblies: two A_2L_3 triple-helical complexes with SO_4^{2-} and PO_4^{3-} , and an A_5L_5 pentagonal macrocycle with CO_3^{2-} . Quantitative binding studies, structural transformation experiments, host–guest encapsulation of betaine, and photo-irradiation experiments collectively demonstrate a multi-stimuli-responsive system whose structural state can be precisely programmed by chemical or optical inputs.

2. Results and Discussion

2.1 Ligand Design, Synthesis, and Characterization

Ligand **L** was designed to satisfy several geometric and functional requirements for anion-templated self-assembly. The C_2 -symmetric trans-stilbene core imposes a well-defined angular relationship between the two hydrazone–urea arms, and the rigidity of the conjugated backbone restricts conformational flexibility, thereby reducing the entropic penalty associated with self-assembly. The urea groups serve as the primary anion-binding units through bifurcated $\text{N}-\text{H}\cdots\text{anion}$ hydrogen bonds, while

the acylhydrazone N–H and imine C–H provide auxiliary binding contacts that increase overall binding valency. The nitrophenyl substituents on the urea nitrogen enhance N–H acidity, thereby strengthening hydrogen-bond donation.

L was synthesized via a convergent multistep route starting from 2-nitrobenzaldehyde and dimethyl trans-stilbene-4,4'-dicarboxylate (Scheme S1). The final acylhydrazone condensation between the dihydrazide intermediate (e) and the aldehyde precursor (d) was performed in DMF in the presence of catalytic trifluoroacetic acid at 40°C, furnishing L as a yellow solid in 72% yield. The molecular composition of L was confirmed by ¹H NMR spectroscopy (Figure S6) and high-resolution ESI-MS, which showed [L + Na]⁺ at m/z 853.27 (calcd. 853.25), in excellent agreement with the theoretical value (Figure S7).

Single crystals of L suitable for X-ray diffraction analysis were obtained by slow vapor diffusion of diethyl ether into an acetone solution of L containing a trace amount of tetrapropylammonium hydroxide (TPAOH), conducted under light-protected conditions. The crystal structure, solved in an orthorhombic space group, confirmed the anticipated molecular geometry (Fig. 1). Both the central stilbene C = C bond and the two acylhydrazone C = N bonds adopt the all-trans (E,E,E) configuration, yielding an elongated, near-planar molecular conformation. This preorganized geometry is stabilized by an intramolecular hydrogen-bonding network involving the urea N–H, hydrazone N–H, and carbonyl oxygen atoms, as well as intermolecular contacts with the TPA⁺ counterions and hydroxide anions present in the crystal lattice. The solid-state structure establishes unambiguously that the designed C₂-symmetric, rigid scaffold is realized in the free ligand, providing a well-defined starting geometry for anion coordination studies.

Figure 1. Crystal structure of ligand L determined by single-crystal X-ray diffraction (orthorhombic space group; thermal ellipsoids drawn at the 50% probability level). Both the central stilbene C = C bond and the two acylhydrazone C = N bonds are in the all-trans (E,E,E) configuration. Key intramolecular N–H⋯O hydrogen bonds are indicated by dashed lines. TPA⁺ counterions and hydroxide anions present in the crystal lattice are omitted for clarity.

2.2 Anion-Dependent Self-Assembly

The self-assembly behavior of L was systematically investigated with a panel of anions spanning different geometries and charge states: spherical Cl[−], tetrahedral SO₄^{2−} and PO₄^{3−}, trigonal planar CO₃^{2−}, and planar trimesate (1,3,5-benzenetricarboxylate, C₆H₃(COO)₃^{3−}). Complexes were prepared by in situ mixing of L with the appropriate tetraalkylammonium salts in acetone-d₆ or DMSO-d₆ under light-protected conditions, and characterized by ¹H NMR spectroscopy and HR-ESI-MS. A summary of the stoichiometries and key ESI-MS assignments for all characterized assemblies is provided in Table 1.

Table 1
Summary of anion-coordinated assemblies of L: composition, stoichiometry, and key HR-ESI-MS assignments.

Anion	Assembly	Topology	Key ESI-MS Species	m/z (obs.)	m/z (calcd.)
Cl ⁻	A ₄ L	1:4 complex	[(Cl) ₄ LK ₂ Na(TBA)] ⁻	1146.01	1146.10
SO ₄ ²⁻	A ₂ L ₃	Triple helix	[(SO ₄) ₂ L ₃ K(TBA)(CH ₃ CN) ₃ (H ₂ O) ₄] ²⁻	1580.47	1580.52
PO ₄ ³⁻	A ₂ L ₃	Triple helix	[(PO ₄) ₂ L ₃ (TBA) ₄] ²⁻	1825.97	1825.91
CO ₃ ²⁻	A ₅ L ₅	Pentagon	[(CO ₃) ₅ L ₅ Na ₄ K ₃] ³⁻	1554.05	1554.02
C ₆ H ₃ (COO) ₃ ³⁻	A ₂ L ₃ / A ₄ L ₄	Mixture	multiple peaks	—	—

With Cl⁻, ¹H NMR studies in DMSO-d₆ showed characteristic downfield shifts of the urea N–H and hydrazone C–H (Hb) protons, consistent with strong N–H⋯Cl⁻ hydrogen bonding. HR-ESI-MS confirmed a 1:4 (A₄L) stoichiometry (Table 1), typical for halide binding by a bis-urea receptor. With (TBA)₂SO₄ in acetone-d₆, a single sharp ¹H NMR spectrum with a diagnostic symmetric pattern was observed (Fig. 2), indicating the formation of a well-defined symmetric assembly. Pronounced downfield shifts of the N–H and Hb signals confirmed strong anion-binding interactions. HR-ESI-MS revealed an A₂L₃ stoichiometry corresponding to a triple-helical structure (Table 1), in which the C₂-symmetric geometry of L and the tetrahedral coordination sphere of SO₄²⁻ are mutually complementary. Treatment of L with (TBA)₃PO₄ likewise produced an A₂L₃ triple helix confirmed by HR-ESI-MS (Table 1), but with a distinctly different ¹H NMR signature relative to the sulfate analog (Fig. 2), indicating a modified internal geometry arising from the higher charge density and different hydrogen-bond-accepting capacity of PO₄³⁻. By contrast, reaction of L with (TMA)₂CO₃ yielded a sharp, symmetric NMR spectrum distinct from the helicate spectra (Fig. 2) and an HR-ESI-MS pattern consistent with an A₅L₅ macrocycle (Table 1). The trigonal planar geometry and lower charge density of CO₃²⁻ evidently favor cyclic over helical assembly. Finally, addition of trimesate anion produced complex, composition-dependent NMR equilibria and mass spectral evidence for coexisting A₂L₃ helical and A₄L₄ tetragonal species (Figures S14, S25, S26), consistent with the reduced symmetry of the planar tricarboxylate anion impeding single-assembly formation. The structural diversity of these assemblies is schematically summarized in Scheme 1.

Figure 2. ¹H NMR spectra (400 MHz, 298 K) comparing (a) free ligand L in DMSO-d₆ with the three representative anion-coordinated assemblies in acetone-d₆: (b) (TBA)₄[(SO₄)₂L₃], (c) (TBA)₆[(PO₄)₂L₃], and (d) (TMA)₁₀[(CO₃)₅L₅]. Arrows indicate the diagnostic downfield shifts of the urea N–H and hydrazone Hb protons upon anion coordination. The distinct chemical shift patterns confirm that each anion templates a unique supramolecular architecture.

Scheme 1. Schematic representations of the anion-dependent self-assembled architectures of L with diverse anions (Cl⁻, SO₄²⁻, PO₄³⁻, CO₃²⁻, trimesate), the corresponding host–guest complexes, and the

stimulus-triggered structural transformations and betaine release.

2.3 Quantitative Anion-Binding Studies and Thermodynamic Basis for Structural Transformation

To quantify the driving forces underlying the observed assembly preferences, UV-Vis titration experiments were performed in DMF by monitoring changes in the ligand absorption spectrum upon incremental addition of anion salts (Figures S28–S29). The association constants (K_{a}) were determined by nonlinear regression analysis: $K_{\text{a}}(\text{PO}_4^{3-}) = (3.63 \pm 0.35) \times 10^5 \text{ M}^{-1}$ and $K_{\text{a}}(\text{SO}_4^{2-}) = (2.34 \pm 0.41) \times 10^5 \text{ M}^{-1}$. This ordering reflects the higher charge density and superior hydrogen-bond-accepting ability of PO_4^{3-} relative to SO_4^{2-} . The approximately 1.6-fold greater binding affinity of phosphate over sulfate provides a clear thermodynamic driving force for anion-exchange-induced structural interconversion.

Building on this thermodynamic hierarchy, a series of stimulus-triggered structural transformation experiments were performed and monitored by ^1H NMR and HR-ESI-MS (Fig. 3). Upon addition of 2 equivalents of $[\text{K}(\text{18-crown-6})]_3\text{PO}_4$ to a preformed solution of $(\text{TBA})_4[(\text{SO}_4)_2\text{L}_3]$ in acetone- d_6 , the ^1H NMR signals characteristic of the sulfate triple helix gradually disappeared over several hours at room temperature and were replaced by a new signal set identical to that of an authentic sample of $[\text{K}(\text{18-crown-6})]_6[(\text{PO}_4)_2\text{L}_3]$ (Fig. 3a). HR-ESI-MS confirmed the complete disappearance of sulfate-containing assemblies and the exclusive formation of the phosphate triple helix (Figure S37). Analogously, the $(\text{TMA})_{10}[(\text{CO}_3)_5\text{L}_5]$ pentagon was quantitatively converted to the phosphate triple helix upon addition of phosphate (Fig. 3b, Figure S35), and the sulfate helix could be converted to the carbonate pentagon by addition of $(\text{TMA})_2\text{CO}_3$ (Figure S31–S33), demonstrating the reversibility and programmability of the transformation network. These results confirm that anion exchange provides a versatile and thermodynamically controlled mechanism for switching between discrete supramolecular states.

Figure 3. Anion-exchange-driven structural transformation monitored by ^1H NMR (400 MHz, acetone- d_6 , 298 K). (a) Transformation of $(\text{TBA})_4[(\text{SO}_4)_2\text{L}_3]$ to $[\text{K}(\text{18-crown-6})]_6[(\text{PO}_4)_2\text{L}_3]$ upon addition of 2 equiv $[\text{K}(\text{18-crown-6})]_3\text{PO}_4$. (b) Transformation of $(\text{TMA})_{10}[(\text{CO}_3)_5\text{L}_5]$ to $[\text{K}(\text{18-crown-6})]_6[(\text{PO}_4)_2\text{L}_3]$ upon addition of phosphate. The complete replacement of the original spectral signals by those of the product assembly confirms quantitative transformation in both cases.

2.4 Host–Guest Chemistry and Stimulus-Responsive Guest Release

The internal cavities of the triple-helical assemblies were investigated for their ability to encapsulate small cationic guest molecules. Phosphate complexes prepared with different tetraalkylammonium counterions showed a clear size-selectivity: ^1H NMR spectra of $(\text{TMA})_6[(\text{PO}_4)_2\text{L}_3]$ and $(\text{TEA})_6[(\text{PO}_4)_2\text{L}_3]$ each exhibited an additional upfield-shifted signal near 2.56 ppm attributable to encapsulated TMA^+ or TEA^+ within the shielded helical cavity (Figures S10, S13), whereas complexes with the larger TPA^+ and TBA^+ counterions showed no such signal, indicating that the cavity diameter selectively accommodates cations up to the size of TEA^+ .

Guided by this size selectivity, we investigated the encapsulation of betaine (trimethylglycine), a biologically relevant zwitterion whose trimethylammonium group closely resembles TMA⁺ in steric profile. A striking host-selectivity was observed (Fig. 4). Addition of betaine to (TBA)₄[(SO₄)₂L₃] produced two distinct sets of methyl signals: one corresponding to free betaine in solution and a second, markedly upfield-shifted set at 2.54 ppm attributable to betaine encapsulated within the sulfate helical cavity (Fig. 4a). Complementary HR-ESI-MS analysis confirmed the formation of a betaine-encapsulated assembly (Fig. 4d). UV-Vis titration yielded a binding constant of $K = (1.6 \pm 0.26) \times 10^5 \text{ M}^{-1}$ (Figure S41), consistent with a moderately strong host-guest interaction. In stark contrast, addition of betaine to [K(18-crown-6)]₆[(PO₄)₂L₃] produced no upfield-shifted guest signals (Fig. 4b), indicating that encapsulation does not occur in the phosphate helix. This differential behavior is attributed to the more electrostatically polarized and structurally compact internal environment of the phosphate helix, arising from the stronger anion-template interactions that leave insufficient space and reduced hydrophobic character for betaine accommodation.

This host-selectivity was exploited to construct a prototype anion-exchange-triggered release system. The betaine-loaded complex (TBA)₄[(SO₄)₂L₃]⊃betaine was prepared, and 2 equivalents of [K(18-crown-6)]₃PO₄ were added to the solution. Sequential ¹H NMR monitoring revealed the progressive disappearance of signals from both the sulfate helix and encapsulated betaine, concurrent with the appearance of signals corresponding to the phosphate helix and free betaine in solution (Fig. 4c). This result directly demonstrates that phosphate-induced structural transformation from the sulfate to the phosphate helix liberates the encapsulated betaine guest, providing a proof-of-concept for chemically triggered guest release driven by competitive anion binding.

Figure 4. Host-guest chemistry and stimulus-triggered betaine release. (a) ¹H NMR spectra (400 MHz, acetone-d₆, 298 K) showing betaine encapsulation in (TBA)₄[(SO₄)₂L₃]: the upfield-shifted methyl signal at δ 2.54 ppm (marked with asterisk) confirms inclusion within the helical cavity. (b) ¹H NMR spectra confirming absence of betaine encapsulation in [K(18-crown-6)]₆[(PO₄)₂L₃]; only free betaine signals are observed. (c) ¹H NMR monitoring of phosphate-triggered betaine release from (TBA)₄[(SO₄)₂L₃]⊃betaine upon addition of [K(18-crown-6)]₃PO₄, showing disappearance of the encapsulated betaine signal and emergence of free betaine. (d) HR-ESI-MS spectrum of the betaine-encapsulated assembly (TBA)₄[(SO₄)₂L₃]⊃betaine.

2.5 Photo-Responsive Disassembly

Beyond chemical stimuli, ligand L incorporates two orthogonal photoswitchable units: the central stilbene C = C bond and the two acylhydrazone C = N bonds, both of which undergo E-to-Z isomerization upon UV irradiation. The photo-responsiveness of all anion-coordinated assemblies was investigated by irradiation with 365 nm UV light.

Upon irradiation for 24–36 hours, all three assemblies—(TBA)₄[(SO₄)₂L₃], (TMA)₁₀[(CO₃)₅L₅], and (TBA)₆[(PO₄)₂L₃][−]underwent dramatic spectral changes by ¹H NMR, converging to similar post-irradiation spectra irrespective of the original anion (Fig. 5a). The vinyl proton H1 (C = C) shifted

downfield from approximately 7.4 ppm to approximately 7.9 ppm, and the imine proton H_b (C = N) shifted downfield to approximately 10.0 ppm. These chemical shift changes are diagnostic for E-to-Z isomerization of both the C = C and C = N bonds, as the altered bond geometry modifies the local magnetic anisotropy environment of neighboring protons²⁷.

UV-Vis spectroscopy provided complementary evidence for the photo-induced conformational changes (Fig. 5b). Before irradiation, (TBA)₄[(SO₄)₂L₃] exhibited a strong absorption band at 350–360 nm, assigned to the n→π transition of the C = N bonds and the π→π transition of the extended conjugated system. After 36 hours of 365 nm irradiation, this band decreased substantially in intensity, while absorption near 210 nm increased concomitantly. These reciprocal intensity changes are consistent with disruption of the extended π-conjugation and alteration of the transition dipole moment geometry upon isomerization from planar trans to bent cis configurations, which reduce cofacial stacking and exciton coupling within the helical assembly.

The most definitive evidence for light-induced disassembly came from HR-ESI-MS analysis of irradiated samples (Figures S46–S48). After prolonged UV irradiation, mass spectra of all three complexes showed complete disappearance of peaks corresponding to the original A₂L₃ or A₅L₅ assemblies. Instead, new peaks were observed and assigned exclusively to mononuclear ligand–anion adducts: [(PO₄)LNaK(H₂O)][–] at m/z 1006.50 (calcd. 1006.18) for the irradiated phosphate complex; [(CO₃)LK(H₂O)(C₃H₆O)₂(CH₃CN)₂][–] at m/z 1145.70 (calcd. 1145.35) for the carbonate complex; and [(SO₄)L(NH₄)(H₂O)₄][–] at m/z 1016.77 (calcd. 1016.28) for the sulfate complex. The uniform collapse of all assemblies to 1:1 ligand–anion adducts confirms that the primary photochemical event is E-to-Z isomerization of the ligand itself, which subsequently disrupts the preorganized hydrogen-bonding geometry required for multi-component self-assembly.

DFT calculations (B3LYP-D3/6-31G(d), IEFPCM/DCE) were performed on L in all relevant isomeric configurations to rationalize the photo-disassembly mechanism (Fig. 5c)^{28–29}. The all-trans (E,E) isomer is the global energy minimum, while the all-cis (Z,Z) configuration is the highest in energy (Table S1). The computed HOMO–LUMO energy gap for the (E,E) isomer (3.58 eV, corresponding to approximately 346 nm) is in reasonable agreement with the 365 nm excitation wavelength used experimentally, given the inherent approximations of the DFT methodology and the complexity of the actual photophysical transitions. Critically, because L contains two distinct photoactive double bonds (C = C and C = N) that isomerize at different quantum efficiencies, complete thermal reversion to the all-trans state is kinetically hindered under ambient conditions. The resulting long-lived mixed-isomer population maintains a sufficient proportion of Z-containing isomers to prevent reassembly of the supramolecular architectures, providing a mechanistic basis for the irreversibility of photo-disassembly observed under the present experimental conditions.

Figure 5. Photo-responsive disassembly of anion-coordinated assemblies. (a) ¹H NMR spectra (400 MHz, acetone-d₆, 298 K) of (TBA)₆[(PO₄)₂L₃] before (bottom) and after (top) 365 nm irradiation for 26 h, showing diagnostic downfield shifts of the vinyl proton H₁ (C = C) and imine proton H_b (C = N) consistent

with E-to-Z isomerization. (b) UV-Vis spectra of $(\text{TBA})_4[(\text{SO}_4)_2\text{L}_3]$ before (solid line) and after (dashed line) 365 nm irradiation for 36 h, showing the decrease of the $n \rightarrow \pi/\pi \rightarrow \pi$ absorption at 350–360 nm and concomitant increase near 210 nm. (c) DFT-optimized structures (B3LYP-D3/6-31G(d)) of the five isomeric configurations of L; relative energies (kcal/mol) are indicated, confirming the (E,E,E) all-trans isomer as the global minimum.

3. Conclusion

We have designed, synthesized, and comprehensively characterized a C_2 -symmetric multifunctional ligand L that integrates urea-based anion coordination, acylhydrazone dynamic covalent chemistry, and dual stilbene/hydrazone photoswitching within a single molecular scaffold. The key findings of this work are fourfold. First, anion geometry and charge density act as decisive templates directing L into topologically distinct supramolecular architectures: tetrahedral SO_4^{2-} and PO_4^{3-} promote A_2L_3 triple-helical assembly, while trigonal planar CO_3^{2-} favors an A_5L_5 pentagonal macrocycle. Second, the thermodynamic hierarchy $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$ in anion-binding affinity enables anion-exchange-driven, quantitative interconversion between all assemblies, demonstrating the programmability of structural state through chemical inputs. Third, the sulfate triple helix selectively encapsulates betaine within its hydrophobic cavity, and phosphate-triggered structural transformation releases the guest in a controlled fashion, establishing a proof-of-concept stimulus-responsive delivery system. Fourth, 365 nm UV irradiation induces concurrent E-to-Z isomerization of both C = C and C = N bonds, disrupting the preorganized hydrogen-bonding geometry and driving complete disassembly of all complexes to mononuclear ligand–anion adducts, as supported by NMR, UV-Vis spectroscopy, mass spectrometry, and DFT calculations. Together, these results establish a multi-stimuli-responsive supramolecular platform with independently addressable chemical and photochemical control inputs, offering a versatile blueprint for the future development of smart materials with applications in molecular sensing, controlled drug delivery, and functional molecular machinery.

Declarations

CRedit Author Contributions

Jinhua Qiao: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Conflict of Interest Statement

The author declares that there are no financial or non-financial competing interests or potential conflicts of interest that could inappropriately influence, bias, or compromise the conduct, analysis, or reporting of the research presented in this manuscript.

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Author Contribution

Jinhua Qiao: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

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Data Availability

The datasets generated and/or analysed during the current study, including the detailed characterization spectra (NMR and UV-Vis), continuous titration profiles, and crystal structure coordinates, are not deposited in a public repository. These data are maintained by the corresponding author as part of an ongoing research programme and are available upon reasonable request. All enquiries regarding data access should be directed to the corresponding author at qiaojinhua2026@163.com.

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Figures

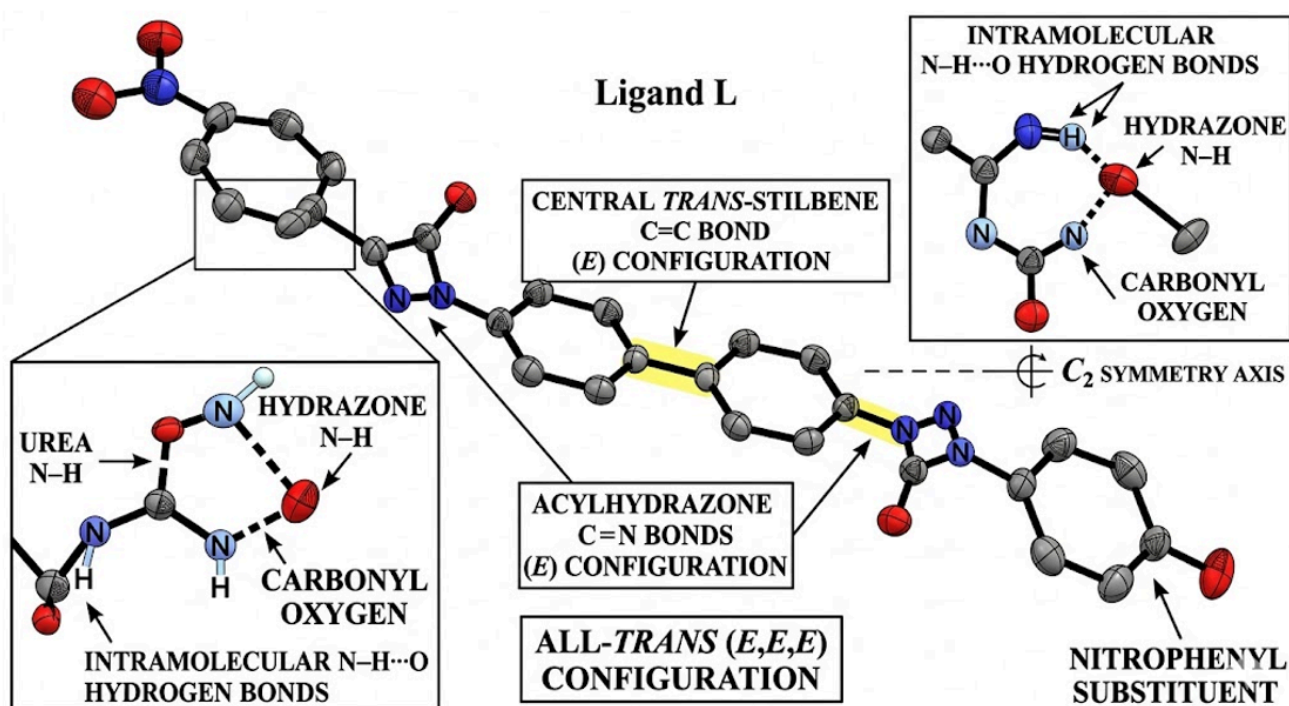


Figure 1

The proposed theoretical framework illustrating the psychological empowerment mechanism linking digital literacy training to college students' mental health outcomes.

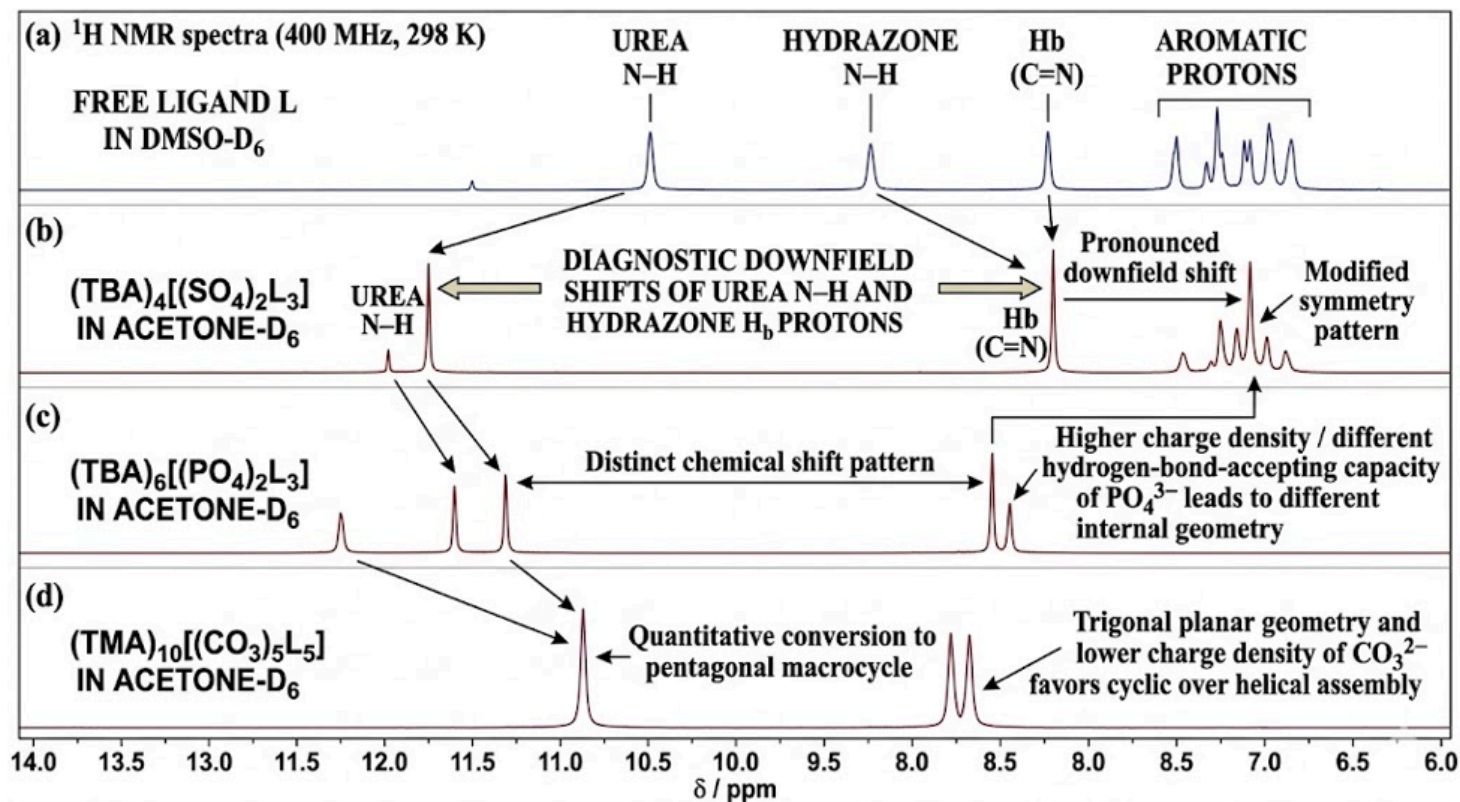


Figure 2

2: .1 Structural framework of the proposed deep learning model for tobacco leaf maturity intelligent recognition and its training validation workflow.

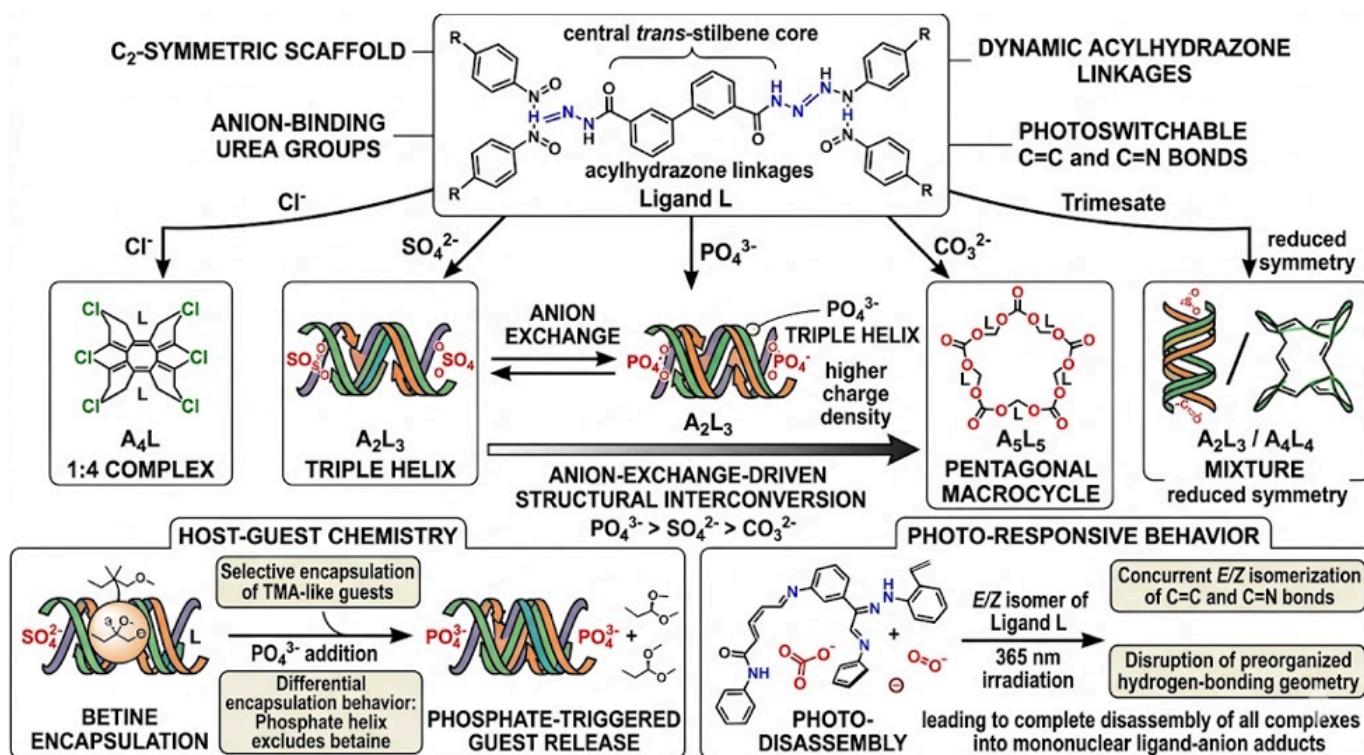


Figure 3

2.:2 Visualization of the intelligent maturity recognition and classification results on test tobacco leaf samples using the proposed deep learning model.

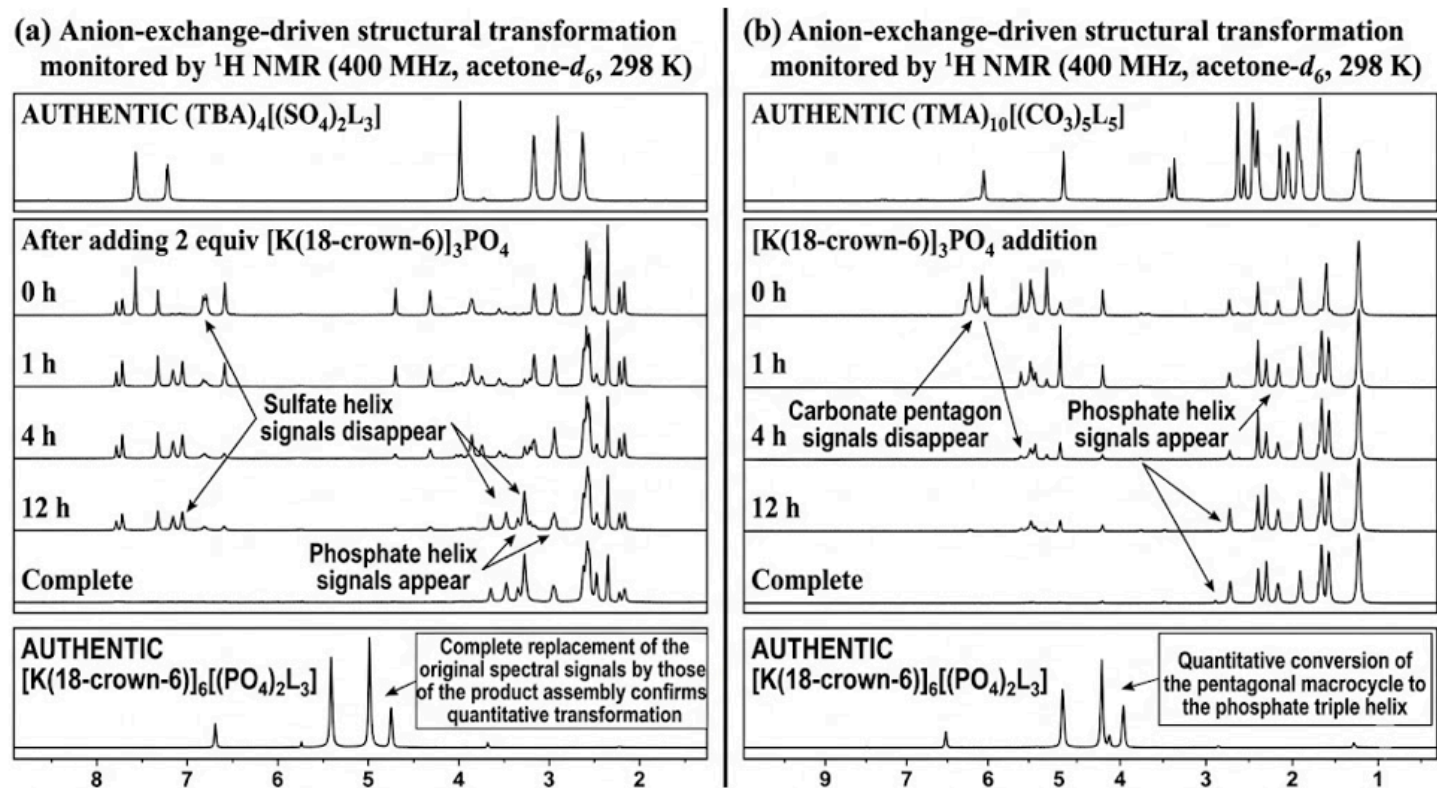


Figure 4

3: Training and validation loss and accuracy curves of the deep learning model for tobacco leaf maturity recognition across different learning epochs.

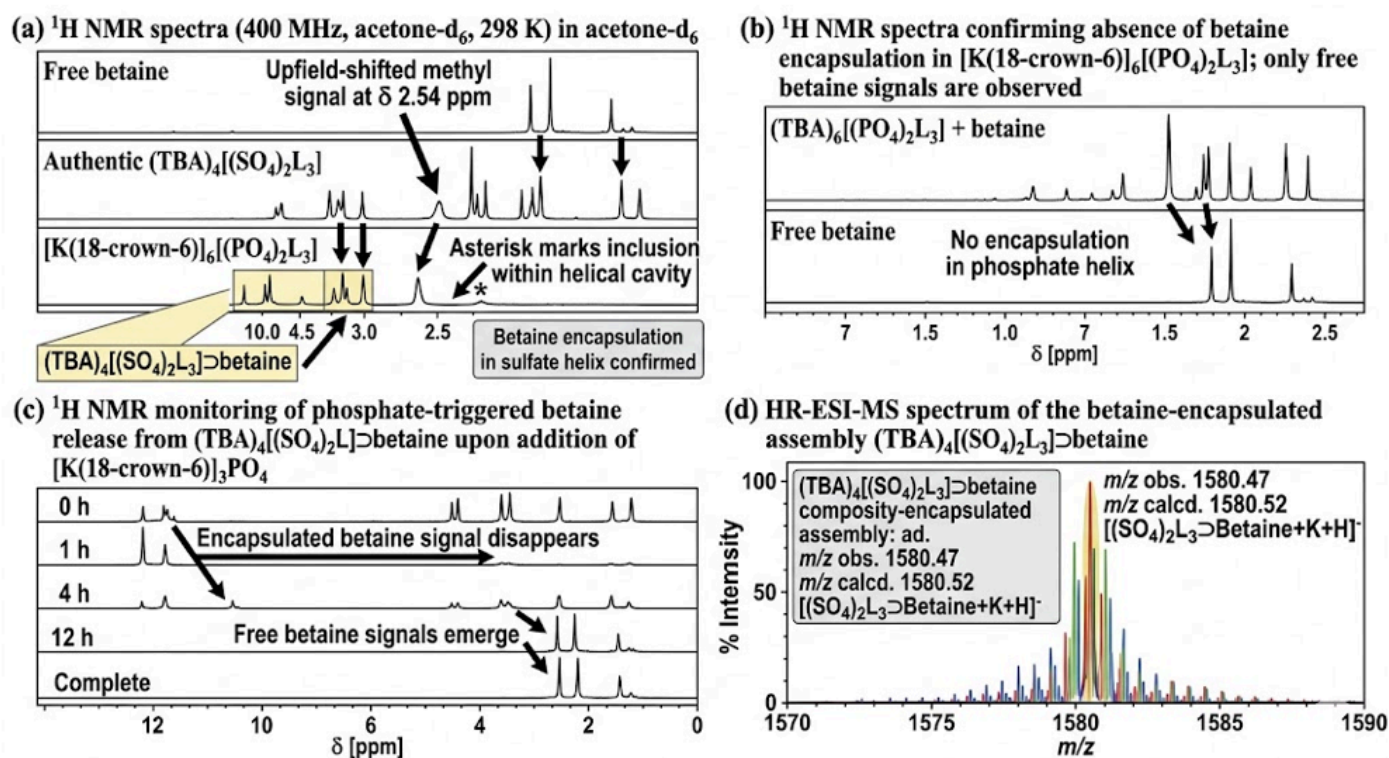


Figure 5

4: Confusion matrix of the proposed deep learning model illustrating the classification performance across different tobacco leaf maturity levels.

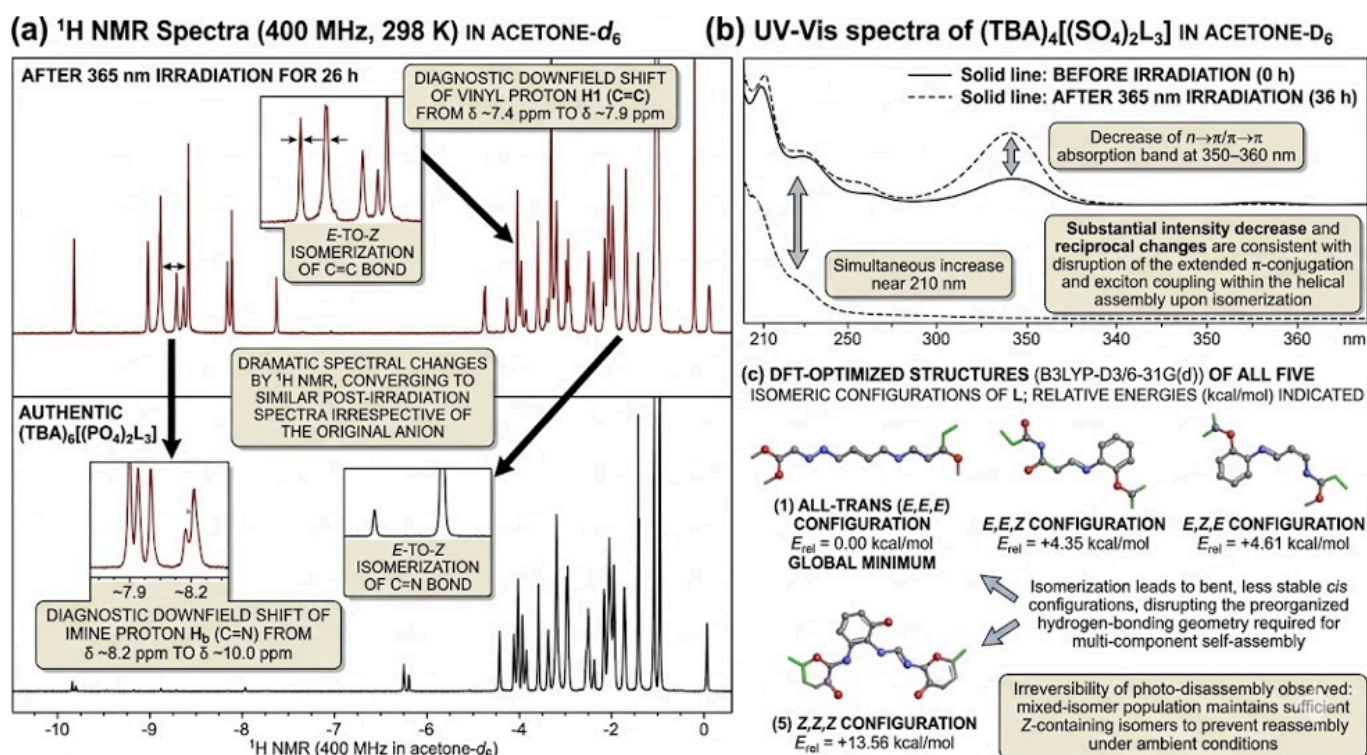


Figure 6

5. Photo-responsive disassembly of anion-coordinated assemblies. (a) ^1H NMR spectra (400 MHz, acetone- d_6 , 298 K) of $(\text{TBA})_6[(\text{PO}_4)_2\text{L}_3]$ before (bottom) and after (top) 365 nm irradiation for 26 h, showing diagnostic downfield shifts of the vinyl proton H1 (C=C) and imine proton Hb (C=N) consistent with E-to-Z isomerization. (b) UV-Vis spectra of $(\text{TBA})_4[(\text{SO}_4)_2\text{L}_3]$ before (solid line) and after (dashed line) 365 nm irradiation for 36 h, showing the decrease of the $\text{n} \rightarrow \pi/\pi \rightarrow \pi$ absorption at 350–360 nm and concomitant increase near 210 nm. (c) DFT-optimized structures (B3LYP-D3/6-31G(d)) of the five isomeric configurations of L; relative energies (kcal/mol) are indicated, confirming the (E,E,E) all-trans isomer as the global minimum.

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