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Self-assembly of chiroptical ionic co-crystals from silver nanoclusters and organic macrocycles

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The Challenge in Nanocluster Assembly

- ❖ Traditional methods struggle to control nanocluster co-crystallization (weak intermolecular forces, racemic outcomes).

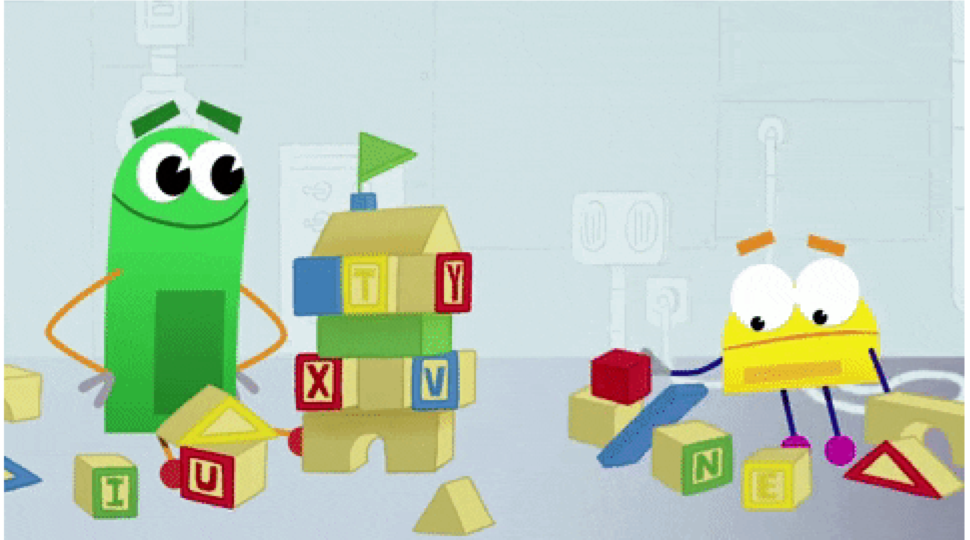
- ❖ No general strategy to engineer solid-state chirality from achiral precursors.

Why It Matters?

Chirality enables advanced technologies:

- Circularly polarized light (CPL) detectors for quantum communication
- Enantioselective catalysis
- Optical computing Current materials: Low dissymmetry factors (g~10−3) limit practicality.

Molecular LEGOs?



Why This Works

•Combines:
◦Atomically precise nanoclusters (uniform size/symmetry)
◦Supramolecular directionality (predictable assembly)
•Key point: Chirality emerges from collective packing, not pre-chiral units.

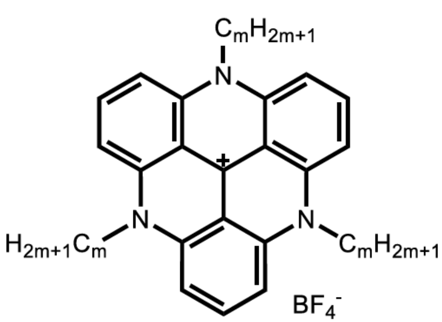
Motivation:

To design and synthesize functional nanocluster-based materials, we sought a class of tunable organic molecules that could direct how nanoclusters and their associated surface ligands pack in the solid state through supramolecular interactions and provide access to unique properties.

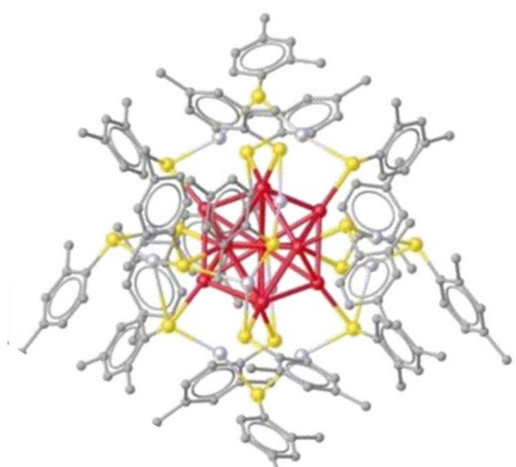
❖ Accordingly, we targeted a subset of platform-based organic macrocycles termed N,N′,N″–trialkyltriazatriangulenes ($TATA^+$)

Design criteria:

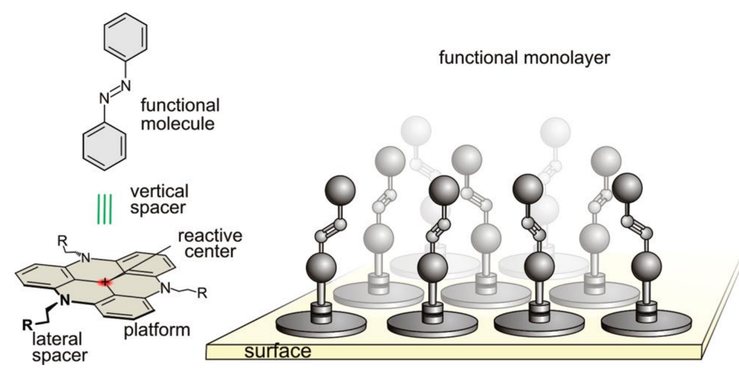
(1) a size that can be easily varied to match the size, shape and symmetry of a given nanocluster;
(2) a symmetric aromatic core surrounded by dangling alkyl groups to provide a balance of structural rigidity and conformational flexibility;
(3) a net positive charge (+1) to fix stoichiometry during co-crystallization with anionic metal nanoclusters;
(4) a highly delocalized charge distribution to allow directional non-covalent interactions with nanoclusters to dominate over non-directional electrostatics; and
(5) a stable chromophore to introduce collective optical phenomena to cluster-based materials.



N,*N*′,*N*″–trialkyltriazatriangulenes ($TATA^+$)



$Ag_{25}(SR)_{18}^-$ (where SR = 2,4-DMBT)



J. Am. Chem. Soc. 2009, 131, 2, 442-443

Introdution with conceptual breakthrough

The Supramolecular Design Core idea: They use cationic TATA+ macrocycles to template anionic $Ag_{25}(SR)_{18}^{-}$ nanocluster.
Key interactions: Marionette-like alkyl chain alignment (−59.5 kcal/mol) CH-π/π-π intraction (−90.9 kcal/mol).

Chirality Emerges Hierarchically

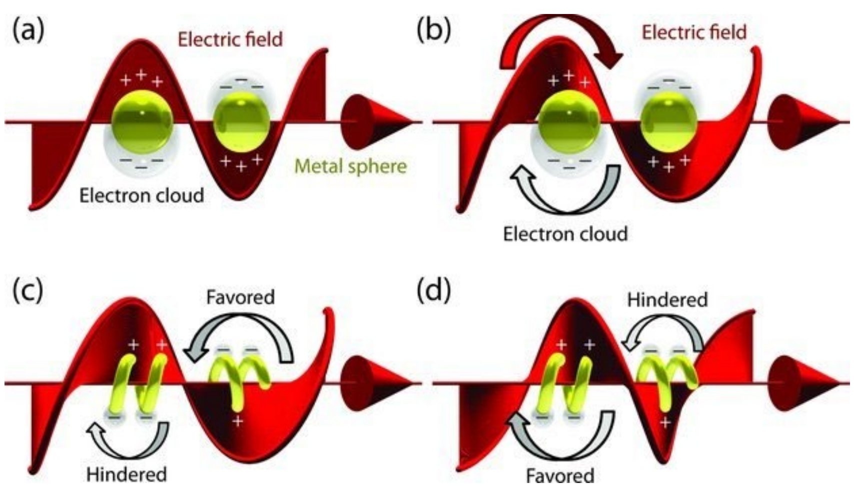
•Achiral TATA+ forms chiral 2D monolayers via alkyl chain rotation.

•These templates enforce homochiral ligand orientations on nanoclusters during co-crystallization.

Synthetic Control

•Varying TATA+ alkyl chain length (C3−C8) tunes:
Nanocluster packing (achiral/racemic → homochiral)
Inter-cluster distances.

Chiroptical effects

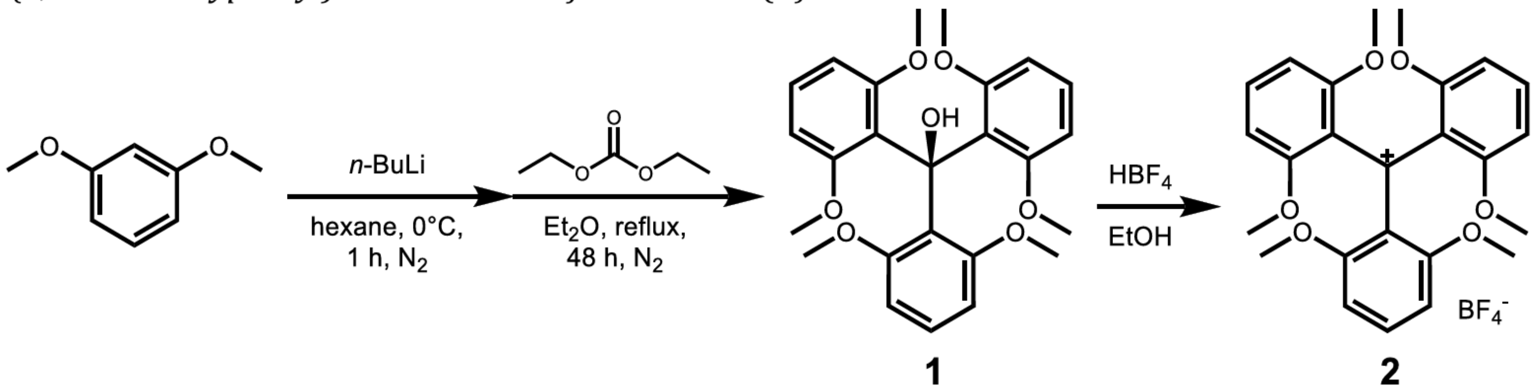


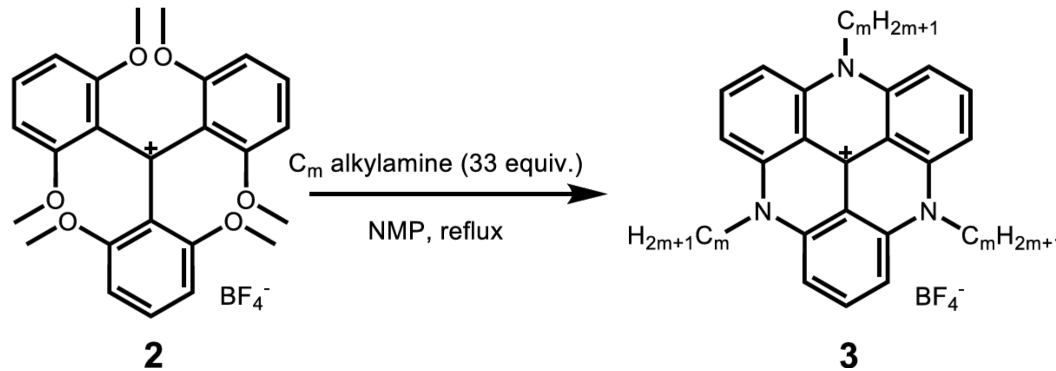
Source: Internet

"Could this approach bypass traditional chiral synthesis in pharmaceutical manufacturing?"

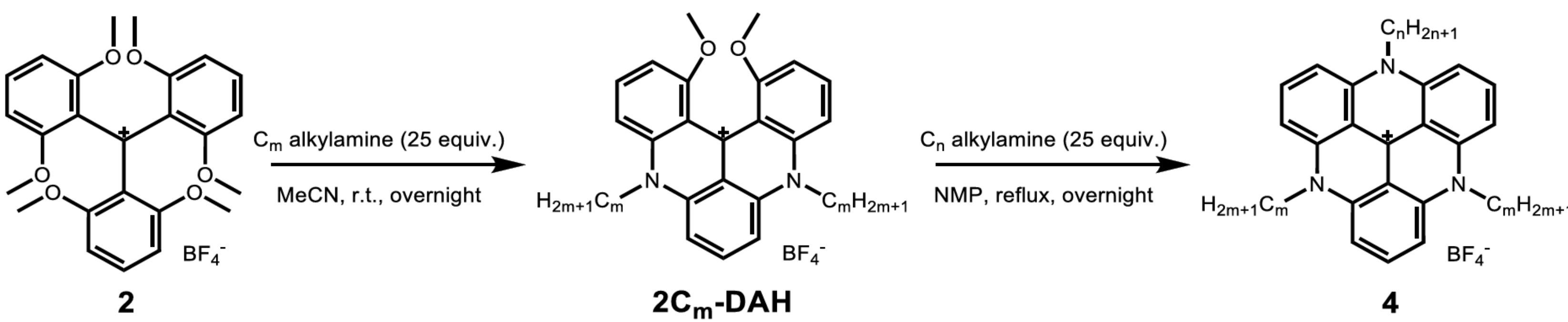
Synthesis of triazatriangulenium tetrafluoroborate ($TATA^+$) salts.

Synthesis of tris(2,6-dimethoxyphenyl)carbenium tetrafluoroborate (**2**)



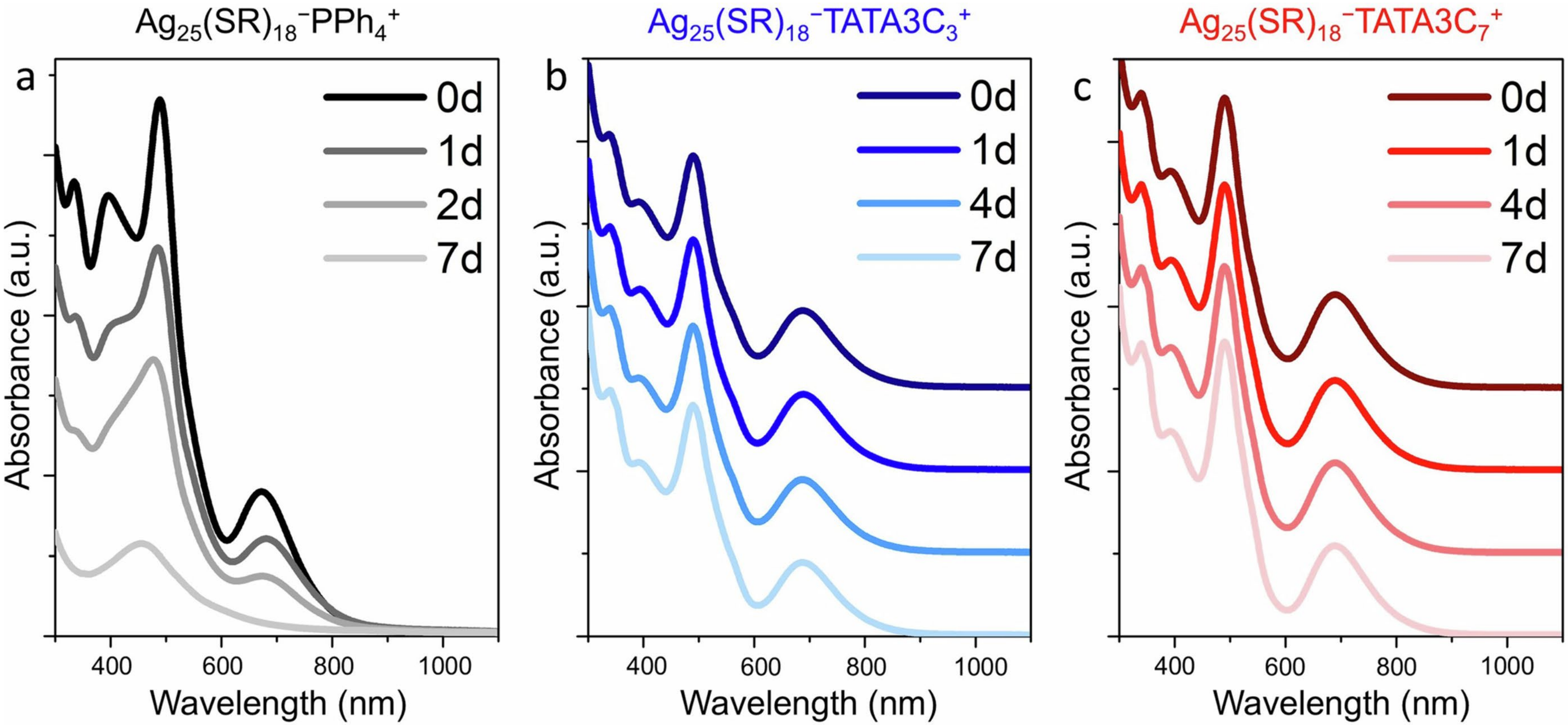


Synthesis of asymmetric TATA2C_m1$C_n$$^+$$BF_4^-$ (**4a–e**):



Results and discussion

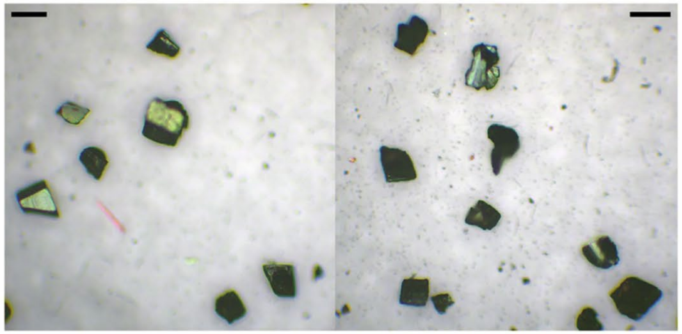
Stability of Ag_{25} clusters with different counterions



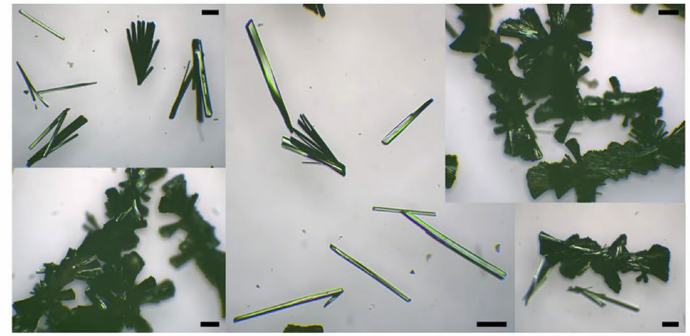
UV-vis-NIR absorption spectra of a, Ag25(SR)18−PPh4+, b, Ag25(SR)18−TATA3C3+, and c, Ag25(SR)18−TATA3C7+ in CH2Cl2 solution at different time points. Spectra in b and c are offset vertically for clarity.

Representative optical images of $NOIC_{25–3Cm}$ ($m = 3–8$)

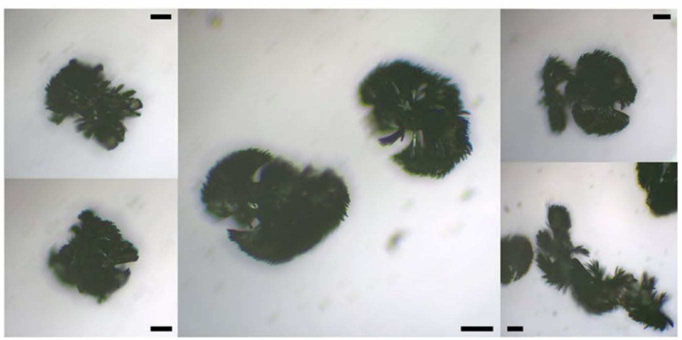
$NOIC_{25–3C3}$



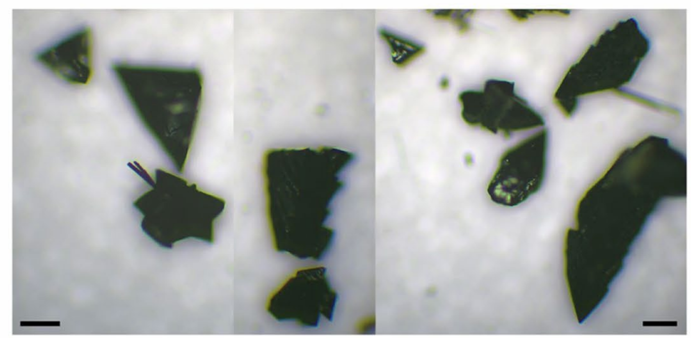
$NOIC_{25–3C4}$



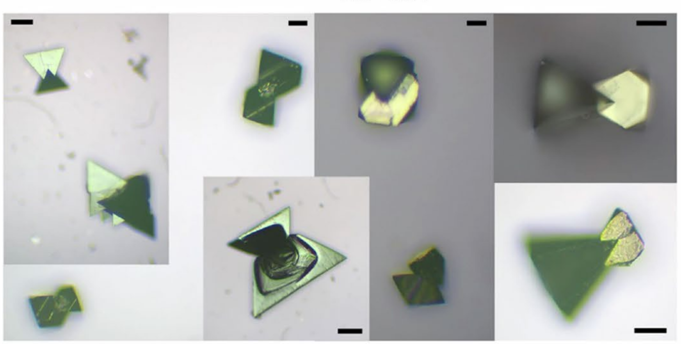
$NOIC_{25–3C5}$



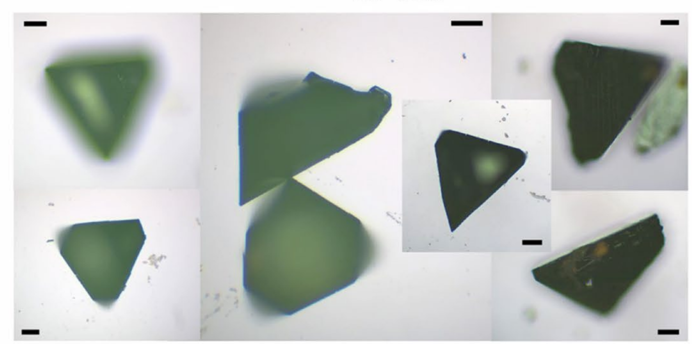
$NOIC_{25–3C6}$



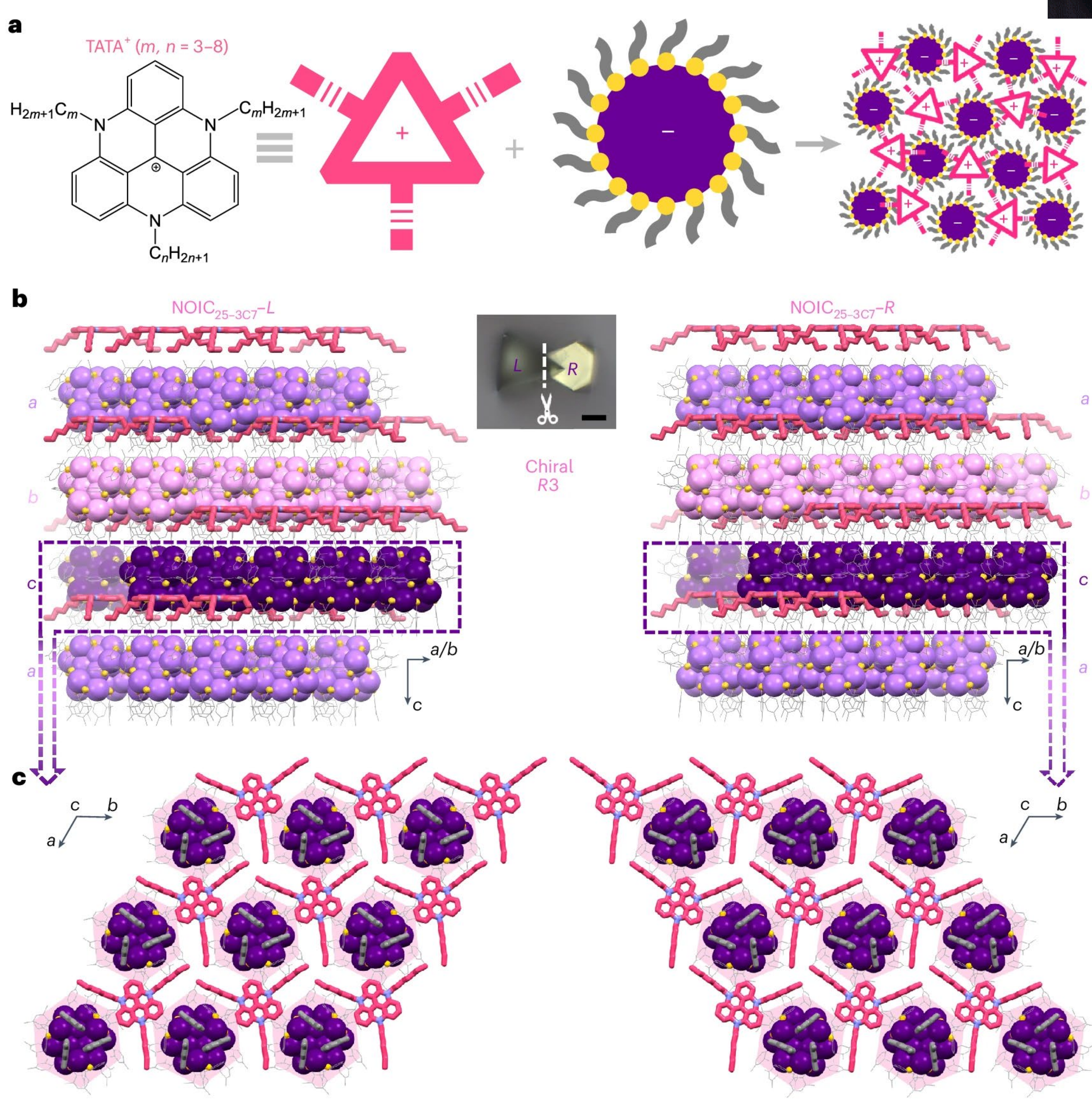
$NOIC_{25–3C7}$



$NOIC_{25–3C8}$



Designing functional NOICs



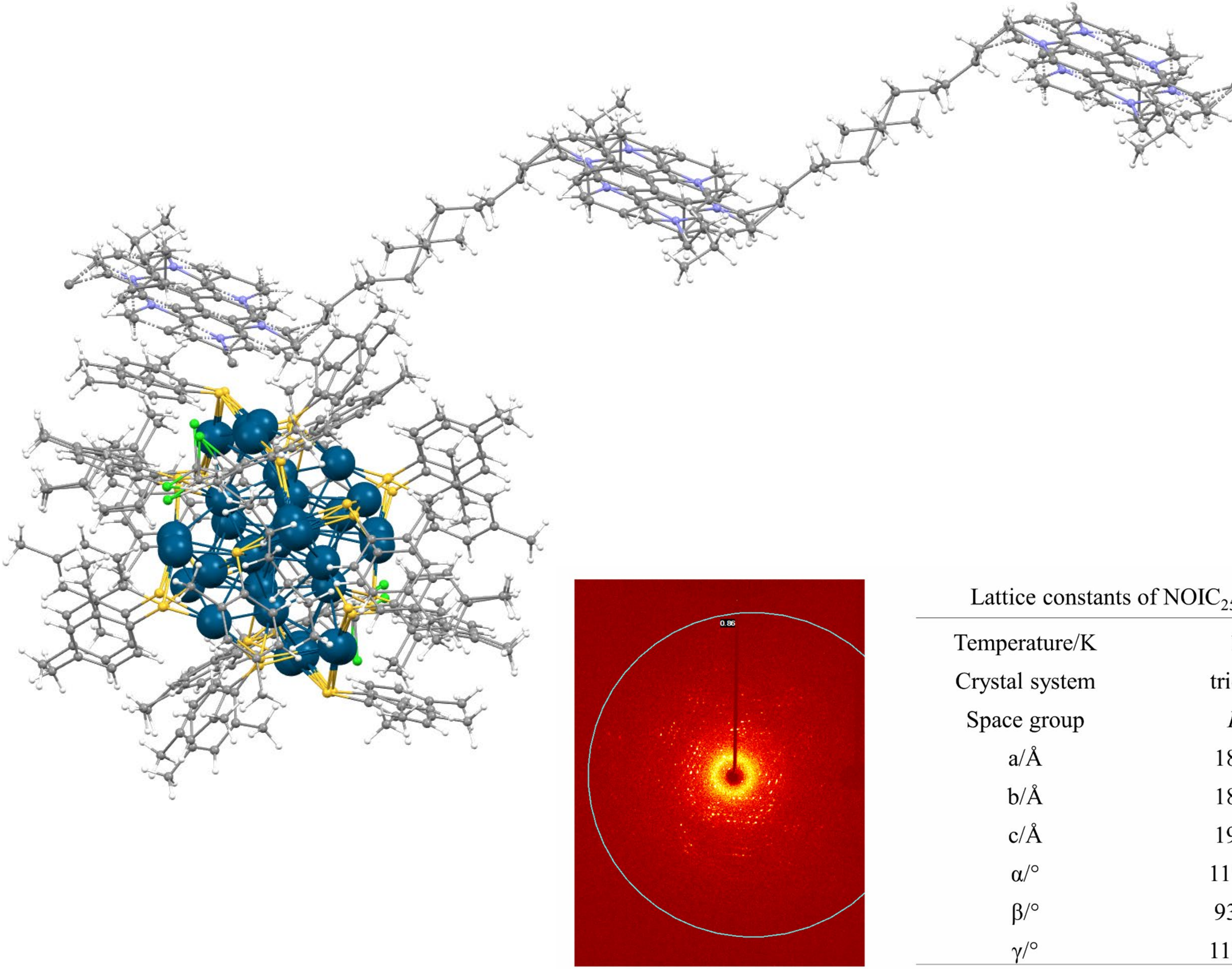
a, Scheme illustrating how $TATA^+$ can be paired with anionic nanoclusters to form NOICs. **b**, Crystal structure of the chiral $NOIC_{25-3C7}$–L(&–R). The inset is an optical image of an enantiomeric pair of $NOIC_{25-3C7}$–L/–R. c, View of the 2D sheets of $TATA3C7^+$ ions and chiral $Ag_{25}(SR)_{18}^-$–L (or –R) within $NOIC_{25-3C7}$. Light blue, N; magenta, C; in $TATA3C7^+$; violet/pink/purple, Ag; in a/b/c layers, yellow, S; grey, C; white, H.

Structural Evidence

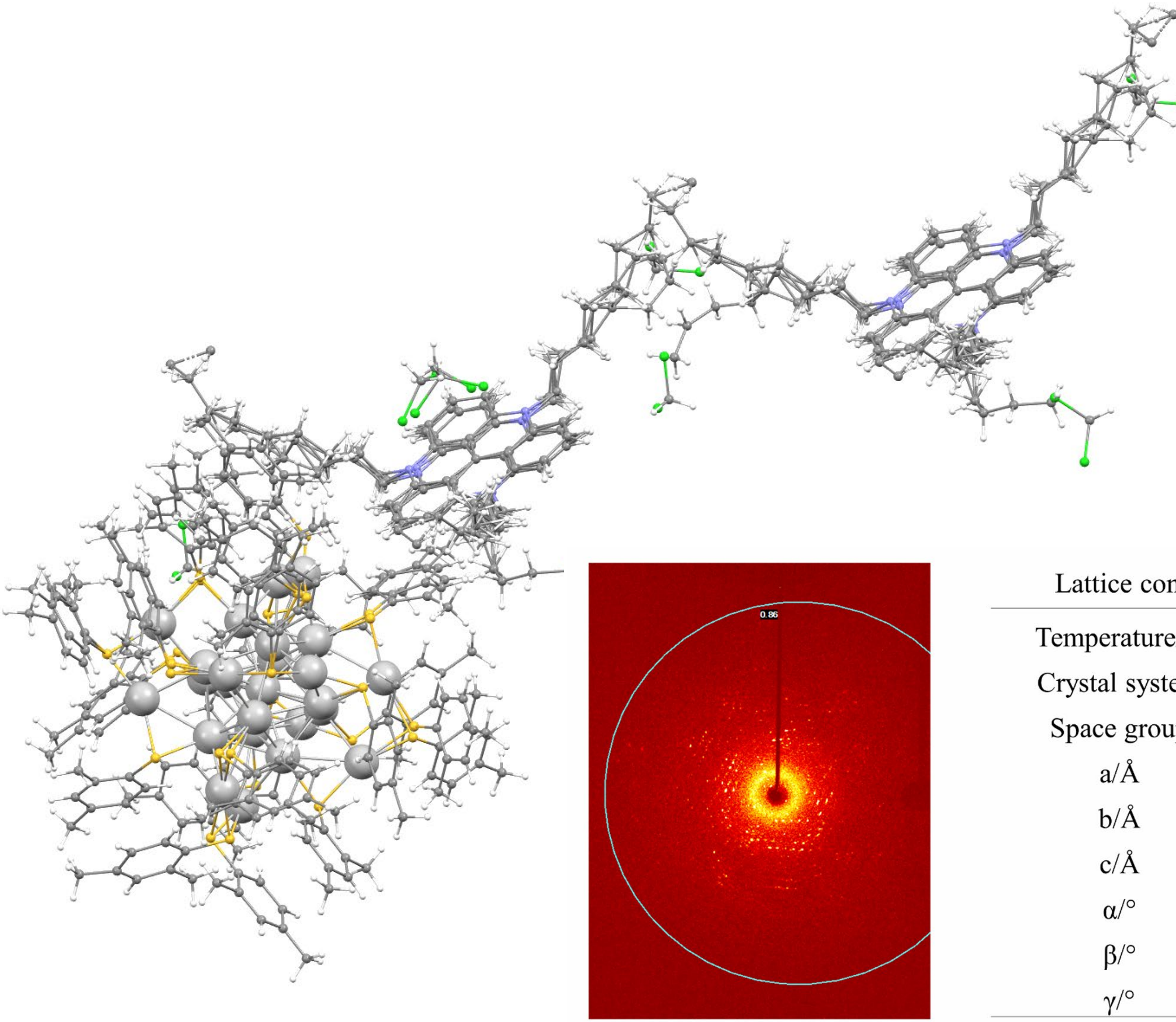
•X-ray crystallography reveals:

◦Homochiral $NOIC_{25-3C7}$ in R3 sp ace group.

◦Racemic $NOIC_{25-3C3}$ vs. achiral $NOIC_{25-2C4,1C8}$.



Lattice constants of $NOIC_{25-2C3,1C8}$	
Temperature/K	100
Crystal system	triclinic
Space group	*P*–1
a/Å	18.080
b/Å	18.542
c/Å	19.753
α/°	117.754
β/°	93.936
γ/°	113.123



Lattice constants of $NOIC_{25-2C3,1C8}$

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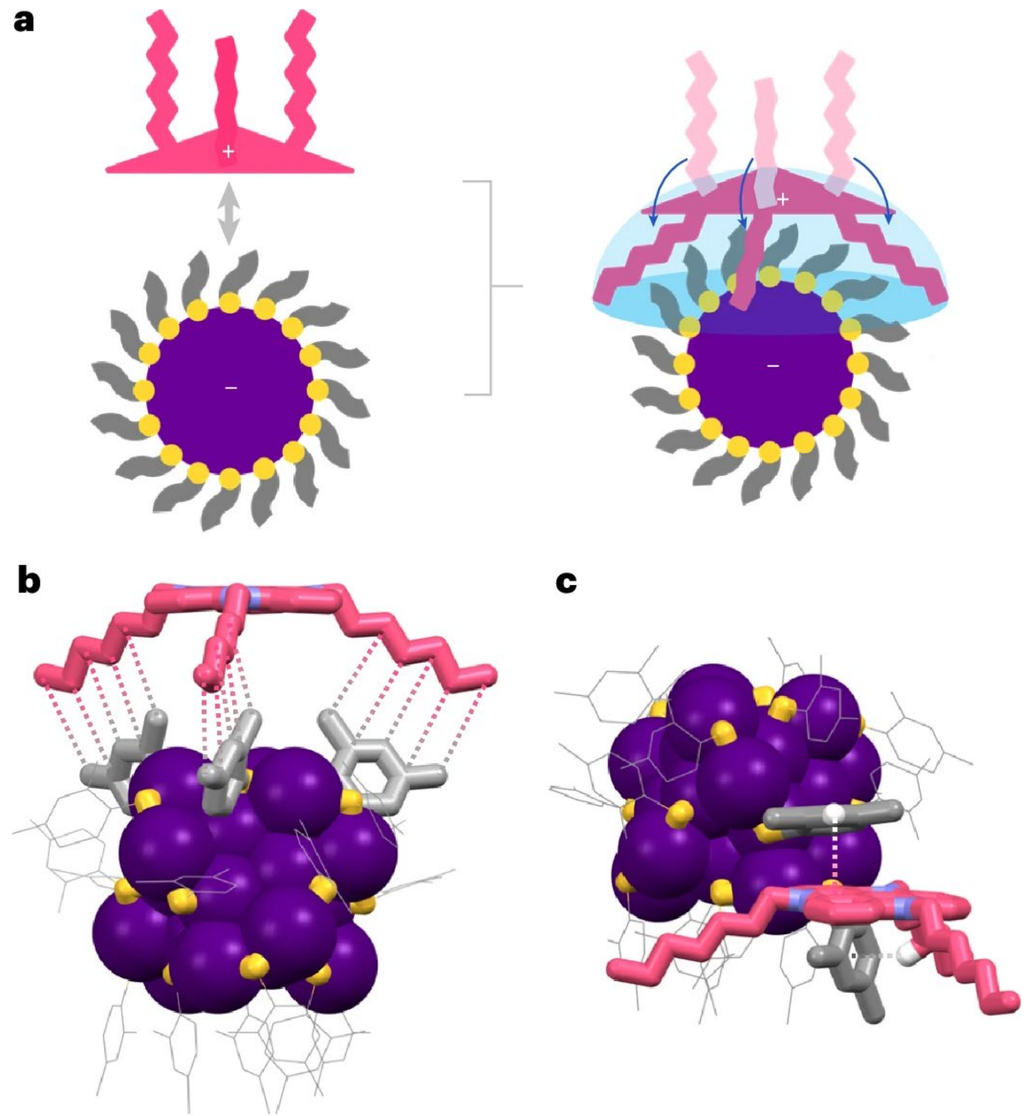
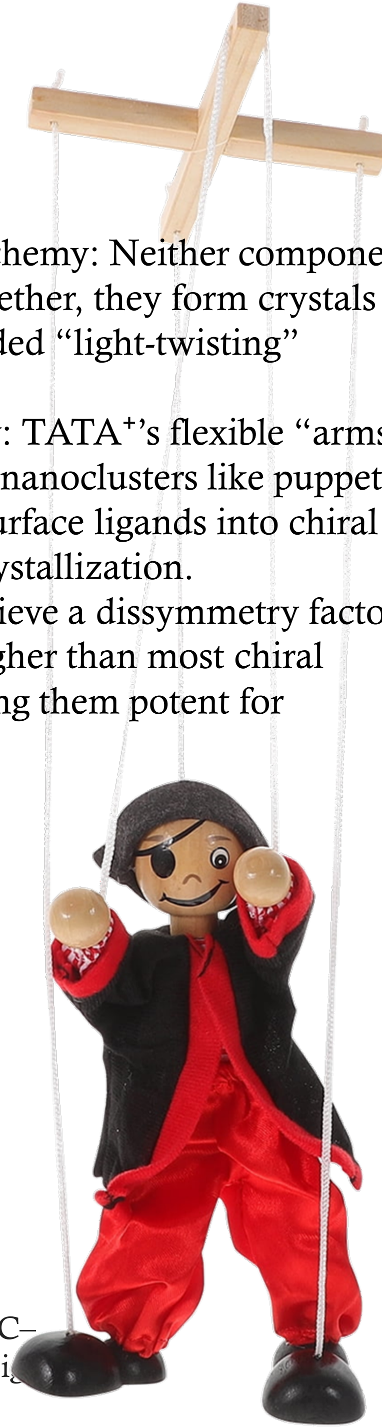
Space group	*P*–1
a/Å	18.080
b/Å	18.542
c/Å	19.753
α/°	117.754
β/°	93.936
γ/°	113.123

Intermolecular interactions within NOICs



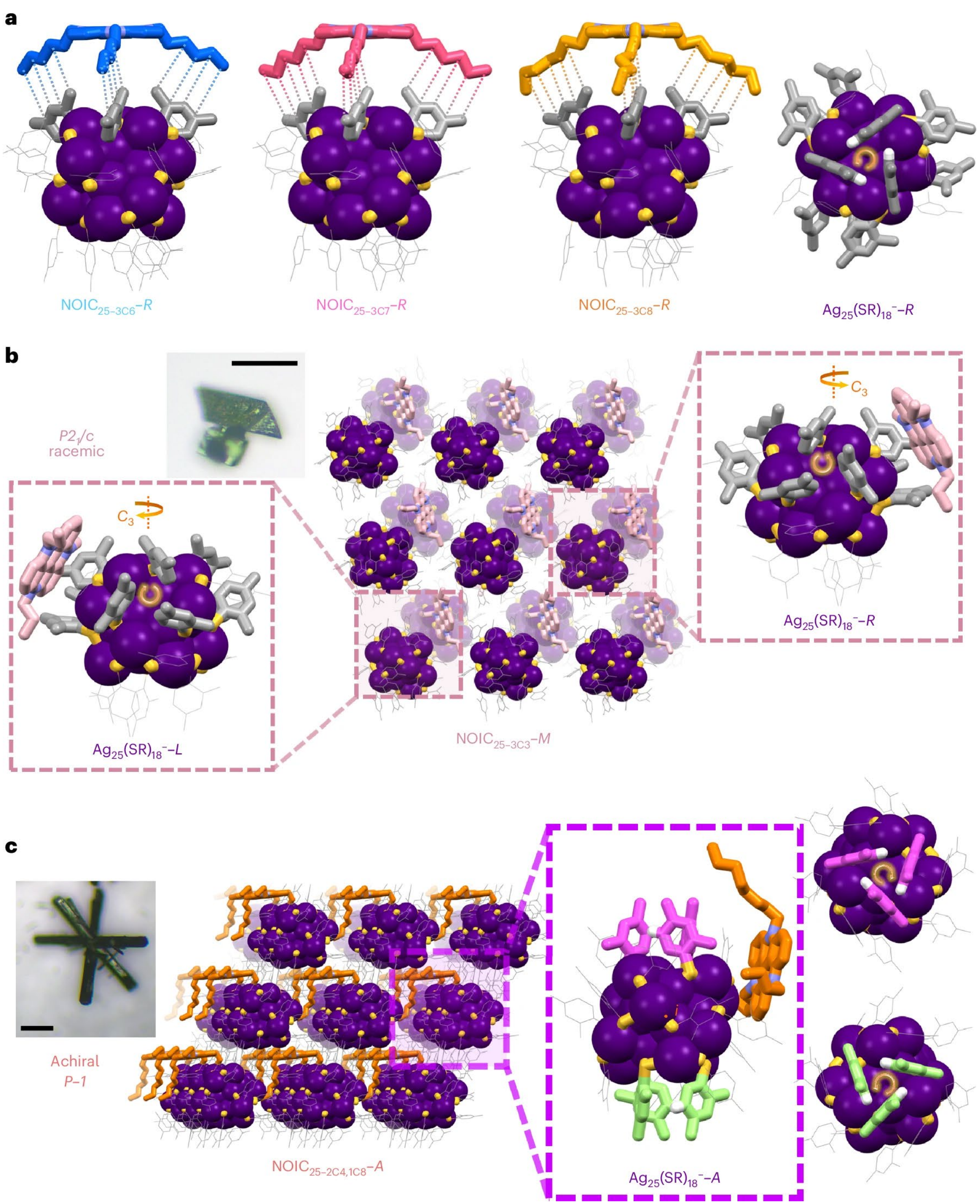
The Twist:

- Achiral → Chiral Alchemy: Neither component is chiral alone, but together, they form crystals with left- or right-handed "light-twisting" abilities.
- Marionette Assembly: $TATA^{+}$'s flexible "arms" (alkyl chains) grip the nanoclusters like puppet strings, forcing their surface ligands into chiral orientations during crystallization.
- These co-crystals achieve a dissymmetry factor (|g|) of 0.15—15× higher than most chiral nanomaterials—making them potent for quantum optics.



a, Illustration of the interaction between $TATA^{+}$ and a spherical nanocluster. **b**,**c**, Marionette-like (**b**) and C–H···π (**c**) interactions between a $TATA3C7^{+}$ molecule and a $Ag25(SR)_{18}^{-}$ nanocluster in $NOIC_{25-3C7}$–*R*. Li
purple, N; magenta, C; in $TATA3C7^{+}$, purple, Ag; yellow, S; grey, C; white, H.

The evolution of chirality in NOICs.



How Chirality Transfers

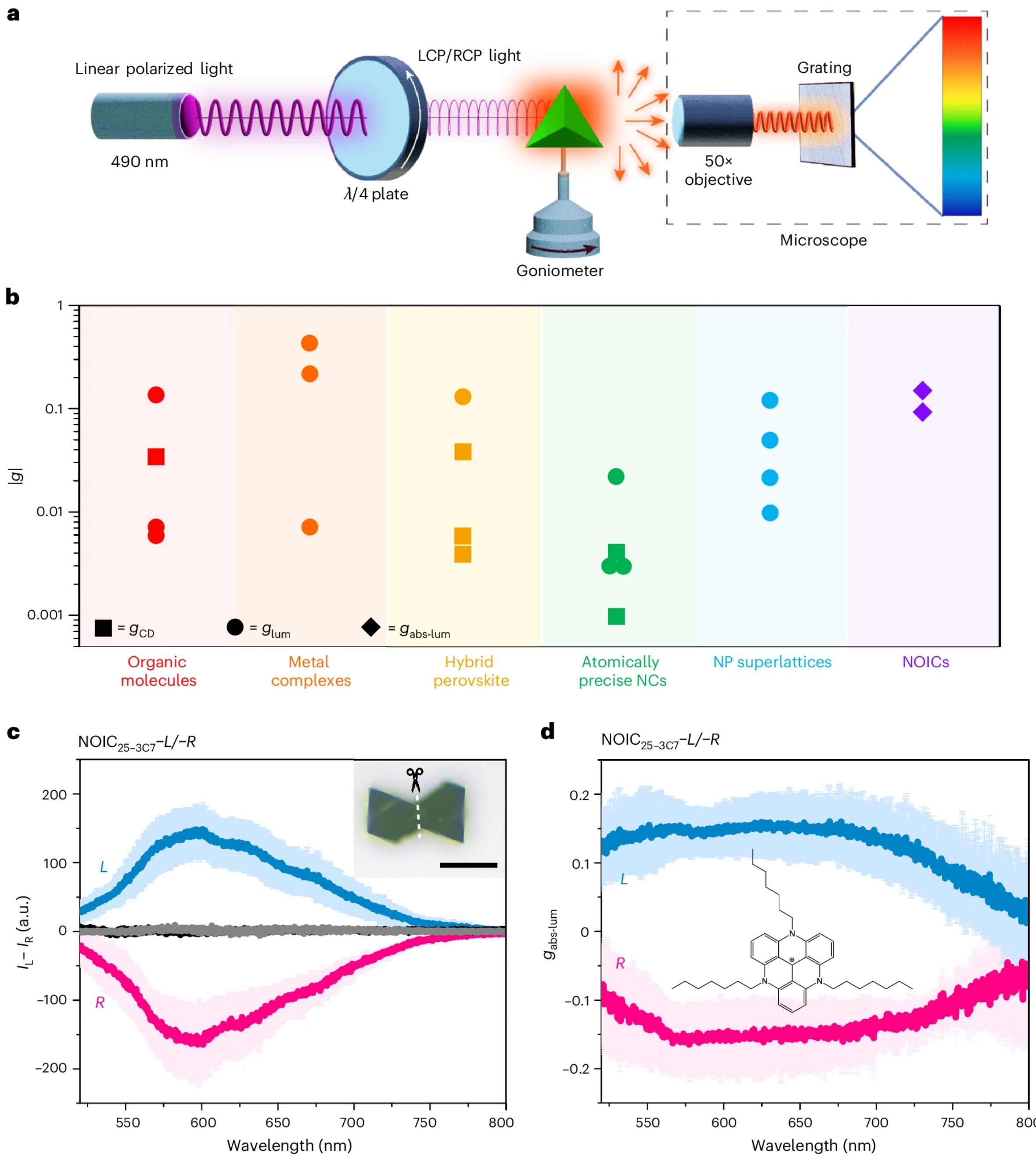
Step 1: TATA+ alkyl chains form chiral 2D monolayers.

Step 2: Marionette interactions "lock" nanocluster ligand orientations.

Step 3: Exciton coupling across TATA layers amplifies dissymmetry.

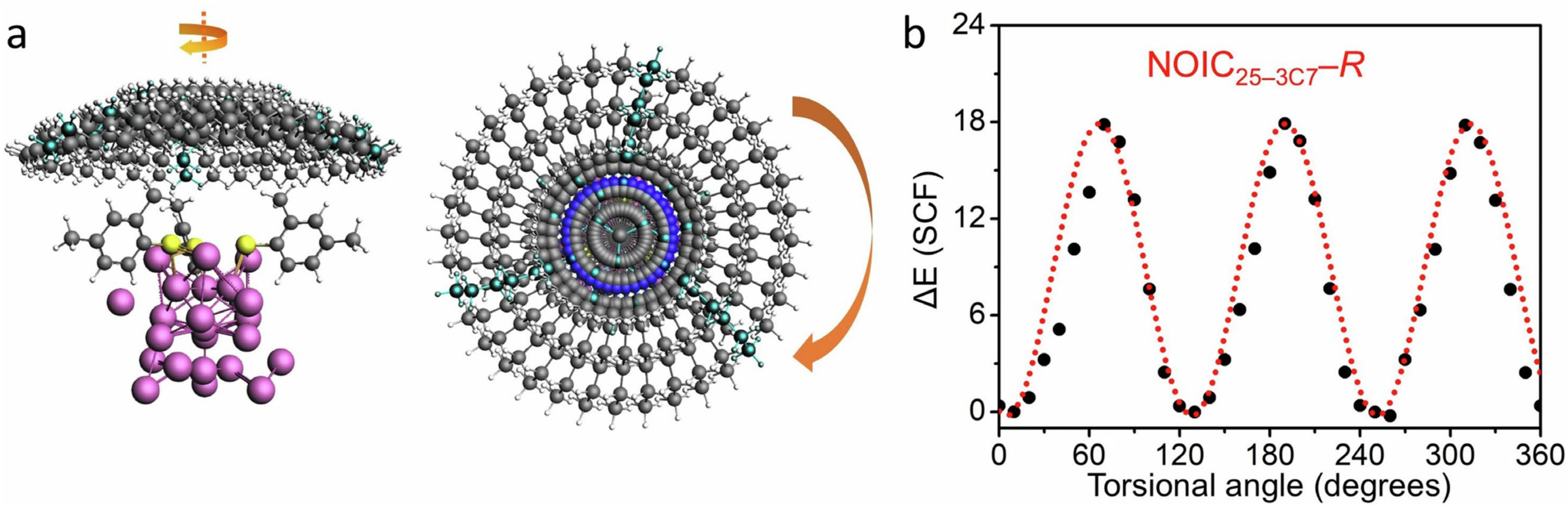
a, The marionette-like interactions in NOIC$_{25-3Cm}$ (m = 6, 7 or 8) are shown along with a representative bottom view of a $Ag_{25}(SR)_{18}^{-}$–R nanocluster within these NOICs. The depicted $Ag_{25}(SR)_{18}^{-}$–R nanoclusters have only right-handed thiolate rotations. **b,** Crystal structure of NOIC$_{25-3C3-M}$ with racemic $Ag_{25}(SR)_{18-}$–R/L pairs. The inset is an optical image of NOIC$_{25-3C3-M}$. **c**, Crystal structure of NOIC$_{25-2C4,1C8-A}$ with achiral $Ag_{25}(SR)_{18-}$–A nanoclusters. The inset is an optical image of NOIC$_{25-2C4,1C8-A}$. The $Ag_{25}(SR)_{18}$−–A nanocluster has both right- and left-handed thiolate rotations. Purple, Ag; yellow, S; light blue, N. Blue, magenta and dark yellow, C in TATA3C6^{+}, TATA3C7^{+} and TATA3C8^{+}, respectively. Pink, orange, C in TATA3C3^{+} and TATA2C41C8^{+}, respectively. Violet/green, C for opposite thiolate rotations in NOIC25−2C4,1C8–A.

Fluorescence-Detected Circular Dichroism (FDCD) of NOICs



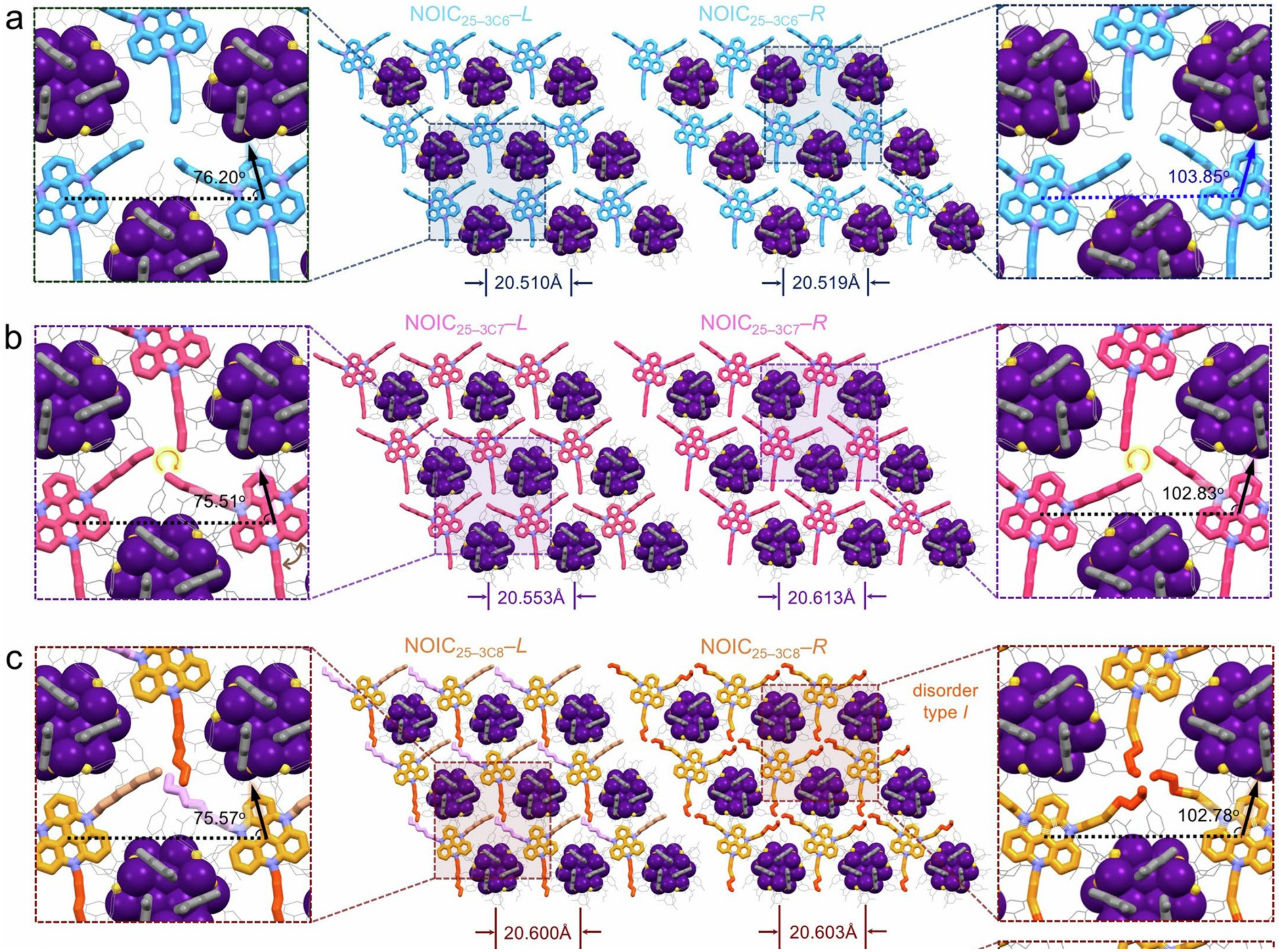
a, Schematic of the FDCD set-up. **b**, Dissymmetry factor of NOICs and other representative chiroptical active materials, **c**, FDCD IL–IR spectra of the L and R enantiomers of NOIC25−3C7 are compared with an amorphous film (grey line) and a solution of dissolved NOIC25−3C7 (black line).
The inset shows an optical image of a pair of L/R co-crystals. Scale bar, 100 μm.
d. Corresponding FDCD $g_{abs\text{-}lum}$ values. The excitation wavelength was 490 nm for all measurements.

Calculated association energy of TATA$^+$ and $Ag_{25}(SR)_{18}^-$–*R*.



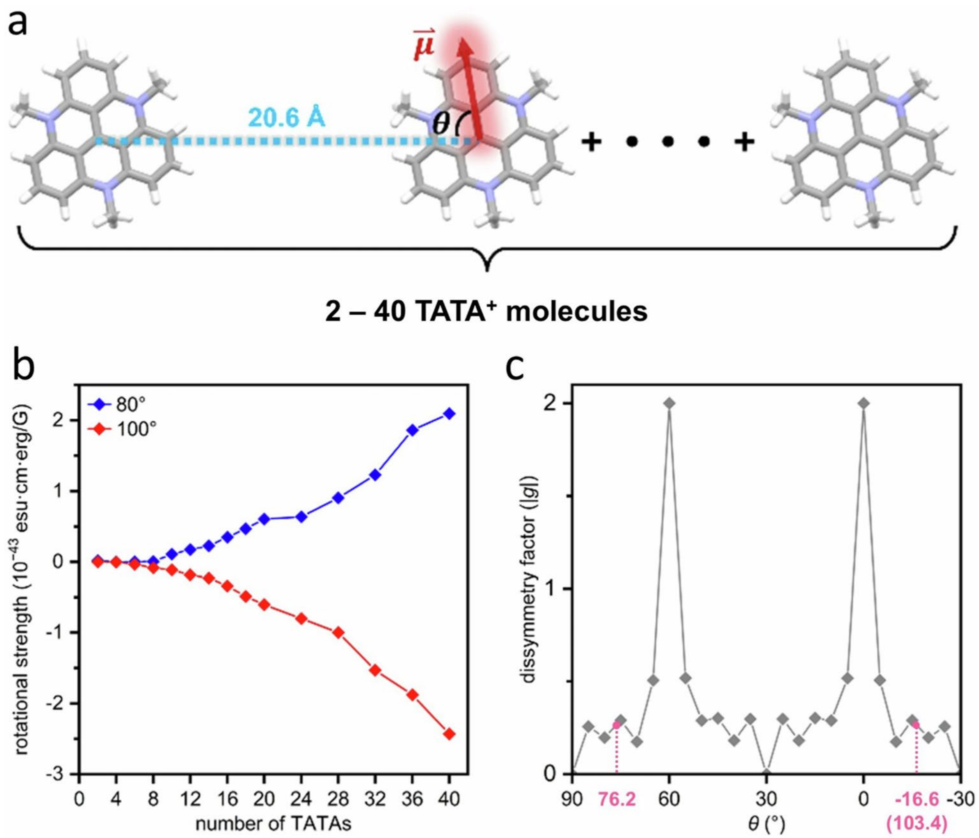
a, Schematic illustration of rotational analysis of a TATA3C7+ residing on a Ag25(SR)18−–*R* nanocluster at every 10°. b, Relative E(SCF) energies (black circles) of the TATA3C7+ and Ag25(SR)18−–*R* pair in NOIC25–3C7–*R* as a function of torsional angle and a fit to the values (red dotted line).

Lattice structures of NOICs with symmetric TATAs



Structures of a, NOIC25−3C6–*L/R*, b, NOIC25−3C7–*L/R* and c, NOIC25−3C8–*L/R*. In TATA3C8+ (panel c), the three C8 chains are disordered among three conformations (marked in different colors) with occupancies of each disorder type = 0.33 for NOIC25−3C8–*L*; the C5–C8 atoms of the three C8 chains (highlighted in orange) are disordered between two conformations with occupancies of both disorder type *I*/*II* = 0.5(3) for NOIC25−3C8–*R*. Color codes: light blue = N, blue/magenta/yellow/orange/pink = C in TATA+; purple = Ag, yellow = S, grey = C. Note that H atoms and CH2Cl2 solvent molecules in the crystal structures are omitted for clarity.

Effect of intermolecular exciton coupling on the dissymmetry factor.



a, A one-dimensional chain of TATA+ molecules with fixed 20.6 Å spacing and a variable angle, θ, between the transition dipole
(red) and vector connecting TATA+ centers (blue). b, Rotational strength vs. number of TATAs in the one-dimensional chain for TATA+ molecules rotated 10° clockwise (θ = 100°, red) or 10° counterclockwise (θ = 80°, blue) away from perpendicular. c, Periodic variation of dissymmetry factor as the angle between the intermolecular vector and transition dipole vector changes. The simulated dissymmetry factor corresponding to the experimental θ is indicated in pink.

Conclusion

- They introduce a supramolecular approach to direct the assembly of atomically precise silver nanoclusters into a series of nanocluster–organic ionic co-crystals with tunable structures and properties.
- Concepts from supramolecular chemistry was adopted to control the assembly of nanoclusters .
- When shorter alkyl chain lengths are used, chiral resolution no longer occurs, and either racemic or achiral co-crystals form.
- The chiral NOICs reported here offer new opportunities for chiroptical devices that can take advantage of the high molar absorptivity of $TATA^+$.