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Induced circular dichroism in phosphine gold(I) arylacetylide urea complexes via hydrogen-bonded chiral co-assemblies

Julien Dubarle-Offner,^[a] Jamal Moussa,^[a] Hani Amouri,^{*[a]} Benjamin Jouvelet,^[a] Laurent Bouteiller,^[a] and Matthieu Raynal^{*[a]}

Abstract: Phosphine gold(I) arylacetylide complexes equipped with a central bis-urea moiety form 1D hydrogen-bonded polymeric assemblies in solution which do not display any optical activity. Chiral co-assemblies are formed by simple addition of an enantiopure (metal-free) complementary monomer. Although exhibiting an intrinsically achiral linear geometry, the gold(I) arylacetylide fragment is located in the chiral environment displayed by the hydrogen-bonded co-assemblies as demonstrated by induced circular dichroism (ICD).

Inducing chirality to metal complexes,^[1] nanoparticles^[2] and surfaces^[3] is a central topic of chemical sciences motivated by important applications in the fields of chiral recognition, sensing, and catalysis. Notably, non-covalent interactions have been designed to place intrinsically achiral metal complexes in the chiral environment provided by various types of chiral species.^[4] Chirality induction is usually confirmed by the presence of a Cotton effect in the spectral region in which only the metal complex absorbs.^[5] The observation of such an induced circular dichroism^[6] (ICD) signal reflects the specific electronic charge distribution within the thus formed chiral supramolecular entities. Gold(I) species have attracted considerable attention since the discovery of their catalytic and spectroscopic properties in solution and their potential use in a wide range of applications.^[7] However, since gold(I) has a known preference for a linear coordination geometry, the induction of chirality in gold(I) complexes is actually a non-trivial task. In the realm of asymmetric catalysis, an effective degree of enantioinduction is observed only for a few classes of chiral covalent ligands or anions.^[8] Alternatively, ICD signals have been observed for achiral gold complexes embedded into chiral surfactants^[9] or self-assembled within a semicrystalline chiral organized structure.^[10] Obviously, the incorporation of gold complexes in other chiral matrices can offer interesting alternatives.^[11] Notably, chiral supramolecular polymers constitute robust platforms for chirality transfer and amplification.^[12] Supramolecular polymers are often in dynamic exchange and co-polymers can be prepared by simply mixing different types of complementary monomers. Since the chiral information is

transferred (and possibly amplified) along the polymeric backbone, co-polymers with a strong helical bias are formed which are composed of two types of monomers: the monomer bearing the chiral information (commonly called the sergeant) and the achiral monomer (the soldier). Up to now, sergeants-and-soldiers experiments have been mostly conducted with structurally-similar monomers in the purpose of probing the chirality amplification properties of supramolecular polymers.^[4e,12]

By adapting the sergeants-and-soldiers principle, we design a new strategy for the incorporation of metal complexes in a dynamic and modular chiral environment in solution. One-dimensional (1D) co-assemblies are targeted which contain sergeants and soldiers that differ not only by their chiral nature but also by the functionality located in their side chain. More precisely, we investigate mixtures containing: i) a bis-urea monomer bearing only the chiral information (the sergeant) and ii) a metal-functionalized bis-urea monomer (the soldier). The two urea moieties, connected through an aromatic spacer, constitute a well-known self-complementary hydrogen-bonded unit for the assembly of 1D supramolecular polymers in solution.^[13] Also, the co-assemblies formed by structurally-simple, non metal-functionalized, sergeants and soldiers are chiral and display strong chirality amplification effects.^[14] We expect that the intrinsically achiral metal fragment, located at the periphery of the co-assemblies, will be a reporter of the chirality displayed by the central supramolecular helices. The formation of such metal-functionalized co-assemblies seems particularly attractive since: it would allow to independently control i) the electronic characteristics of the metal complex soldier and ii) the degree of chirality induction/amplification within the co-assemblies through the design of a metal-free sergeant.

Herein we describe the proof-of-principle of our strategy using racemic gold complexes as the soldiers and enantiopure monomers as the sergeants. The observation of an ICD signal clearly demonstrates that the gold arylacetylide complexes are located in the chiral environment displayed by the co-assemblies. Our investigated gold(I) complexes **1•AuPPh₃** and **1•AuPCy₃** (Chart 1) contain the following structural elements: i) a central bis-urea moiety as associative unit, ii) a racemic 2-ethylhexyl group on one side to impart solubility, iii) a neutral phosphine gold(I) complex on the other side and iv) a rigid 4-phenylacetylene linker in order to prevent interactions between the urea and gold complex units. Neutral metal complexes are particularly adapted for this study since anions have strong affinity for urea functions as exemplified by the well-known anion sensing properties displayed by urea derivatives.^[15]

1•AuPPh₃ and **1•AuPCy₃** were obtained by reacting **1•H** with [AuCl(PPh₃)] and [AuCl(PCy₃)] respectively, in the presence of Cs₂CO₃ and were purified by precipitation in methanol. Analytical data of **1•AuPPh₃** and **1•AuPCy₃** are in accordance

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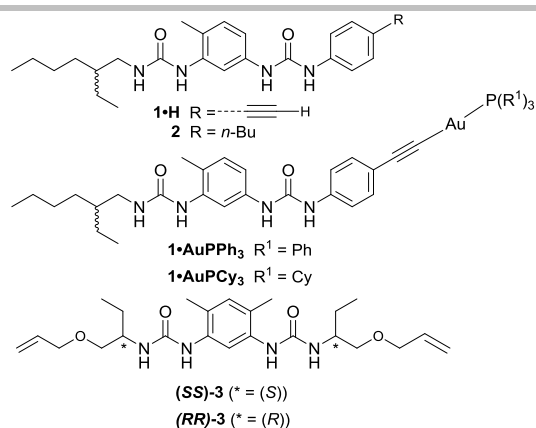


Chart 1 Structure of the bis-urea derivatives.

with the structures drawn in Chart 1 (see the Supporting Information). In particular the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the gold(I) acetylide bis-urea complexes recorded in $[\text{D}_6]\text{-dmsO}$ show a singlet at ca. δ 41.8 ppm and 57.3 ppm respectively. To the best of our knowledge, **1-AuPPh₃** and **1-AuPCy₃** constitute the first examples of metal complexes containing a bis-urea moiety.^[16] **1-AuPPh₃** and **1-AuPCy₃** proved to be well soluble in THF, CH_2Cl_2 and CHCl_3 but very poorly soluble in toluene and cyclohexane. According to these solubility tests, **(SS)-3** and **(RR)-3** were chosen as the enantiopure complementary monomers since these bis-ureas are expected to strongly self-associate even in relatively polar solvents.^[17]

Indeed, Fourier Transform Infrared (FT-IR) spectroscopy and Small Angle Neutron Scattering (SANS) experiments confirm that **(SS)-3** forms long and rigid urea-bonded self-assemblies in $\text{CH}_2\text{Cl}_2/\text{THF}$ 9:1 at mM concentrations (Figure S.1).^[18] Also, the self-assemblies of **(SS)-3** and **(RR)-3** display mirror image CD spectra (Figure S.2). A strong Cotton effect is observed in the region corresponding to aromatic and urea chromophores at $\lambda_{\text{abs}}=232$ nm ($|\Delta\epsilon|=28.0$ L.mol⁻¹.cm⁻¹) and a weak CD signal is also found above 260 nm ($|\Delta\epsilon|\approx 0.5$ L.mol⁻¹.cm⁻¹ at $\lambda_{\text{abs}}=295$ nm). These signals almost totally disappear in ethanol, a strong hydrogen-bond competitor, confirming that the CD activity of **(SS)-3** and **(RR)-3** is related to the supramolecular chirality of the assemblies.

The self-assembly properties of **1-AuPPh₃** and **1-AuPCy₃** in CHCl_3 was also probed by means of FT-IR and SANS analyses. **1-AuPPh₃** and **2**,^[19] a structurally-related bis-urea lacking the phosphine gold(I) acetylide fragment,^[20] present very similar FT-IR spectra with a broad NH band at ca. 3300 cm⁻¹ and a CO band at ca. 1637 cm⁻¹ indicative of the presence of urea-bonded assemblies (Figure 1).^[21] In both cases, small bands related to free NH and CO functions can also be detected (at ca. 3425 cm⁻¹ and 1700 cm⁻¹ respectively) which correspond to the free urea groups located at the extremities of the assemblies and/or to monomers. The same bands are observed for **1-AuPCy₃** but the proportion of free urea groups is higher demonstrating that the assemblies formed by **1-AuPCy₃** are shorter than those of **1-AuPPh₃** as a probable result of higher steric repulsion between consecutive Cy groups in the polymeric structure. Moreover, **1-AuPPh₃** forms discrete cylindrical objects in solution with a radius of 10.1 Å and a length > 250 Å as demonstrated by SANS analysis performed in $\text{CD}_2\text{Cl}_2/\text{THF-d}_8$ (9:1 ratio, Figure S.1). Taken all together, these analyses clearly indicate that the phosphine gold acetylide fragment located at the extremity of **1-AuPPh₃** and **1-AuPCy₃** does not prevent the

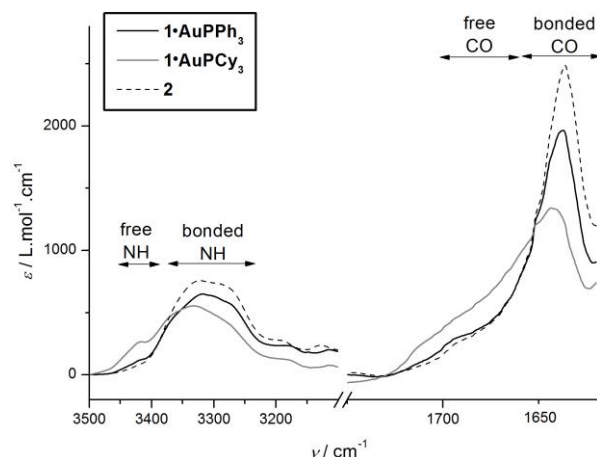


Figure 1 FT-IR spectra of **1-AuPPh₃**, **1-AuPCy₃** and **2** (CHCl_3 , 6 mM). Zoom on the NH and CO bands.

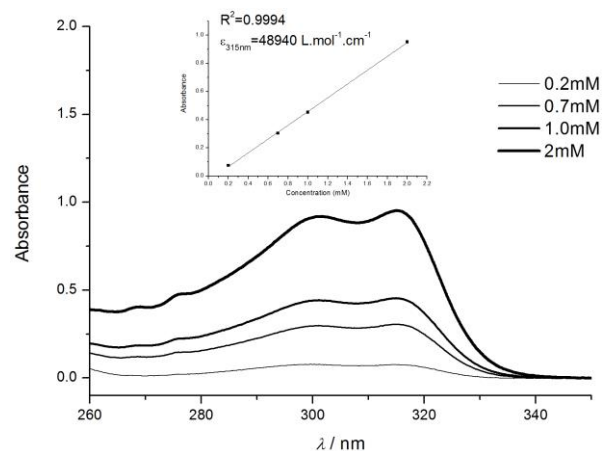


Figure 2 UV absorption spectra of **1-AuPPh₃** (-11°C) in $\text{CH}_2\text{Cl}_2/\text{THF}$ (9:1 ratio) at various concentrations. Inset: linear fitting of the absorbance (measured at $\lambda=315$ nm, 0.1 mm path length) versus the concentration.

association of the central bis-urea units.

We then verified whether the gold(I) acetylide fragment is involved in the self-assembly process of **1-AuPPh₃** and **1-AuPCy₃**. We observed no shifts or shape changes for the absorption bands upon varying the concentration (from 0.2 to 2 mM, Figure 2). This is in contrast to literature examples in which the metal acetylide moiety is involved in the aggregation process through π - π stacking, metal-metal and/or solvophobic interactions.^[5i,5s] The assemblies formed by **1-AuPPh₃** and **1-AuPCy₃** constitute rare examples of gold complexes aggregates in which neither the gold centre nor its connected ligands play a role in the association process.^[22]

1-AuPPh₃ and **1-AuPCy₃** exhibit similar UV absorption spectra in $\text{CH}_2\text{Cl}_2/\text{THF}$ 9:1 (Figure 3). Below 260 nm, both UV spectra show a broad band corresponding to aromatic and urea chromophores (Figure 3). This high-energy absorption band is more intense in the case of **1-AuPPh₃** as the PPh₃ moiety absorbs in this region.^[23] At lower energies, both complexes exhibit structured absorption bands (λ_{abs} at ca. 280, 300 and 315 nm) which closely resemble those displayed by the mono-urea gold(I) acetylide complexes studied by Chao and co-workers.^[16a] Vibrational spacings of ca. 1700 cm⁻¹ and 2200 cm⁻¹ can be ascribed to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}\equiv\text{C})$, respectively (Table S.1). Accordingly, these absorption bands correspond to $^1(\pi\rightarrow\pi^*)$ transitions involving the carbonyl group of the urea functions and the acetylenic unit of the acetylide ligand. The metal-perturbed intraligand (IL) $[\pi\rightarrow\pi^*(\text{C}\equiv\text{C})]$ transition has possibly some metal-

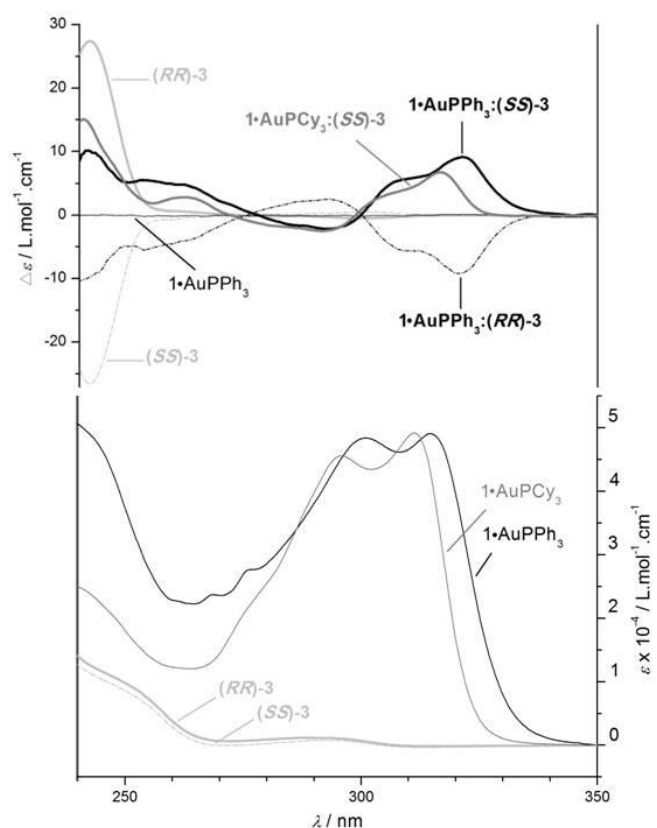


Figure 3 Top: CD spectra (top) of the 1:1 mixtures of the gold complexes and the sergeants, of **(SS)-3**, of **(RR)-3** and of **1•AuPPH₃** (1 mM, CH₂Cl₂/THF 9:1, -11°C). For the mixtures, $\Delta\epsilon = \theta/32980 \times l \times c$ where θ is the measured ellipticity in mdeg, l is the path length in cm and c is the concentration in gold complex in mol.L⁻¹. Bottom: UV absorption spectra of gold complexes and sergeants. The CD spectrum of **1•AuPCy₃** and the UV spectra of the mixtures have been omitted for clarity (see Figure S.3). Color figures in SI.

to-ligand charge transfer (MLCT) character. The low-energy absorption band of **1•AuPPH₃** is slightly bathochromically shifted (3 nm) compared to **1•AuPCy₃** presumably as a result of the different influence of PPH₃ and PCy₃ on the metal-perturbed intraligand (IL) [$\pi \rightarrow \pi^*(C \equiv C)$] transition.^[16a,23-24] As expected given that **1•AuPPH₃** and **1•AuPCy₃** are racemates, their self-assemblies do not show any optical activity (CD spectra, Figures 3 and S.3).^[25]

We next probed the co-assembly properties of soldiers **1•AuPPH₃** or **1•AuPCy₃** with the chiral sergeants **3**. We prepared 1 mM solutions of gold complexes (**1•AuPPH₃** or **1•AuPCy₃**) and sergeants (**(SS)-3** or **(RR)-3**) in CH₂Cl₂/THF (9:1 ratio), a solvent combination in which all partners are soluble, and mixed them in a 1:1 ratio.^[26] The CD spectra of the different mixtures clearly reveal that the soldiers and sergeants form co-assemblies. Indeed, the CD spectra of mixtures of the gold complexes with **(SS)-3** show CD signals which totally differ from that of **(SS)-3** (Figures 3 and S.3). Their CD spectra exhibit: i) a positive peak in the 230-260 nm region, a region in which **(SS)-3** exhibits a strong negative Cotton effect and in which **(SS)-3**, **1•AuPPH₃** and **1•AuPCy₃** strongly absorb, and ii) a weak negative signal followed by a positive signal in the 270-340 nm region in which **(SS)-3** only shows a very weak positive peak. Below 270 nm, the sergeants-and-soldiers co-assemblies and the sergeant self-assemblies exhibit CD signals of opposite signs. Even though the origin of this inversion is difficult to establish given that both aromatic and urea chromophores

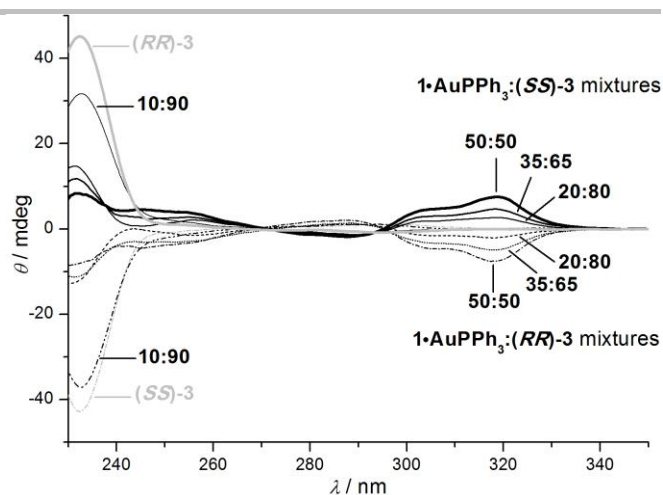


Figure 4 CD spectra of the mixtures of **1•AuPPH₃** and **(SS)-3** or of the mixtures of **1•AuPPH₃** and **(RR)-3** at different ratios (1 mM, CH₂Cl₂/THF 9:1, -11°C). Color figures in SI.

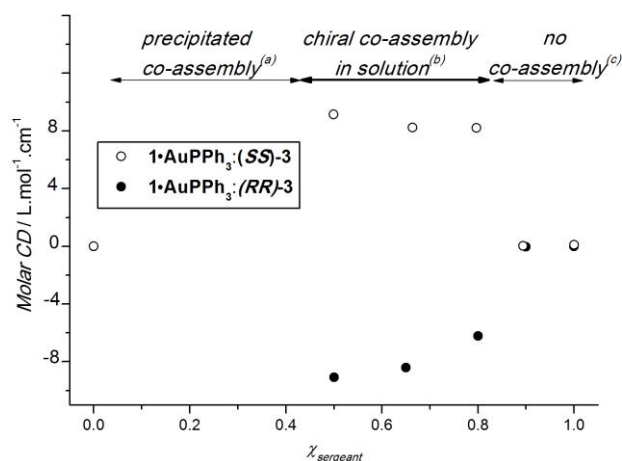


Figure 5 Molar CD ($\Delta\epsilon$, measured at 318.5 nm) vs the ratio of sergeant in the mixtures. $\Delta\epsilon = \theta/32980 \times l \times c$ where θ is the measured ellipticity at 318.5 nm in mdeg, l is the path length in cm and c is the concentration in gold complex in mol.L⁻¹. $\chi_{\text{sergeant}} = [\text{sergeant}] / ([\text{sergeant}] + [\text{gold complex}])$. (a) Social self-sorting between **1•AuPPH₃** and the sergeant but determination of the molar CD values are precluded by the heterogeneous nature of the mixtures. (b) Social self-sorting between **1•AuPPH₃** and the sergeant in solution. (c) Narcissistic self-sorting *i.e.* the individual assemblies formed by **1•AuPPH₃** and the sergeant do not co-assemble.^[27]

absorb in this region, this observation clearly reveals that the bis-urea units of the sergeants-and-soldiers co-assemblies are located in a chiral environment.

Most importantly the bands above 270 nm in the CD spectra of the sergeants-and-soldiers mixtures are related to the transitions observed in the electronic spectra of the gold complexes but not in that of the sergeant (Figure 3). The presence of this ICD signal demonstrates that the peripheral gold arylacetylide fragment of **1•AuPPH₃** and **1•AuPCy₃** are located in the chiral environment displayed by the sergeants-and-soldiers co-assemblies.^[28]

The ICD signal displayed by 1:1 mixture of **1•AuPPH₃** and **(SS)-3** ($\Delta\epsilon_{318.5\text{nm}} \approx 9 \text{ L.mol}^{-1}.\text{cm}^{-1}$) is slightly stronger than that of the 1:1 mixture of **1•AuPCy₃** and **(SS)-3** ($\Delta\epsilon_{314\text{nm}} \approx 6.5 \text{ L.mol}^{-1}.\text{cm}^{-1}$). It might be related to the better association properties of **1•AuPPH₃** (*vide supra*) and/or to the efficiency of the chirality transfer.^[29] Moreover, the CD spectra of **1•AuPPH₃:(SS)-3** and **1•AuPPH₃:(RR)-3** are mirror images showing that the sergeant can be used to invert the chirality induced to the gold arylacetylide fragment (Figures 3 and 4).

We found out that the chirality induced to the intrinsically achiral gold acetylide fragment can be altered in a reversible way by varying the temperature. The ICD signal of the co-assemblies between **1•AuPCy₃** and **(SS)-3** (1:1 mixture) has a maximum intensity at -10°C and -5°C and then gradually decreases, yet a residual ICD signal is still present at 20°C (Figure S.5). More importantly, the initial ICD signal is restored upon returning to the initial temperature (-10°C).

Finally, we probed the influence of the sergeant on the co-assembly process and on the efficiency of the chirality transfer by preparing mixtures of **1•AuPPh₃** and sergeant (**(SS)-3** or **(RR)-3**) at different ratios. We surprisingly found that the mixtures containing more than 50% of gold complex precipitated. Since mixtures are prepared from homogeneous 1mM mother solutions, this observation suggests that the co-assemblies formed but were poorly soluble under these experimental conditions. The CD spectra of the mixtures with a lower amount of gold complex ($\leq 50\%$) are shown in Figure 4. The spectra of the mixtures with 10% of **1•AuPPh₃** resemble those of pure sergeants with a strong Cotton effect at $\lambda_{\text{abs}}=232$ nm and no signal in the 270-340 nm region suggesting that the co-assembly process is hampered in these cases *i.e.* the individual supramolecular polymers formed by **1•AuPPh₃** and **(SS)-3** (or **(RR)-3**) do not co-assemble. In contrast, the mixtures at 20% and 35% of **1•AuPPh₃** exhibit a CD signature which is similar to the one displayed by the mixture containing 50% of **1•AuPPh₃** described above (Figure 3) indicating the formation of chiral co-assemblies.

The molar CD values, defined as the ellipticity normalized by the soldier concentration (**1•AuPPh₃**), can be plotted as a function of the ratio of sergeant in the mixture (Figure 5). For mixtures for which co-assembly is observed in solution ($0.5 \leq \chi_{\text{sergeant}} \leq 0.8$), it is interesting to note that the molar CD values remain approximately constant upon increasing the amount of sergeant. This non-proportional relationship between the molar CD value and the amount of sergeant suggests that the co-assemblies display chirality amplification effects. However, the precipitation of the co-polymers with low sergeant ratio prevents the determination of the minimum amount of sergeant required to get fully chiral co-assemblies. Moreover, as mentioned above, no co-assembly forms for mixtures containing high amount of sergeant. These data indicate that the formation of sergeants-and-soldiers co-assemblies strongly depends on the respective content of gold complex and sergeant present in solution (Figure 5).

In summary, our results clearly demonstrate that phosphine gold(I) arylacetylide fragments, albeit exhibiting an intrinsically achiral linear geometry, can be located in the chiral environment displayed by sergeants-and-soldiers co-assemblies. The chirality induced to the gold acetylide fragment can be inverted by using sergeant enantiomers and altered by varying the temperature holding promising applications in the fields of asymmetric catalysis.^[59,30] The strategy is not limited to gold complexes but can be extended to metal complexes displaying various coordination modes and to other types of functionalized co-assemblies.

Experimental Section

Sample preparation and CD analyses of mixtures of the gold complex and the sergeant: 1.0 mM stock solutions of the gold complex and the sergeant in CH₂Cl₂/THF 9:1 were mixed to the desired ratio and

heated to $-b.p.$ of the solvent. Samples were weighed and corrected for solvent loss when necessary. Samples were briefly heated again a few minutes before CD analyses. CD measurements were performed on a Jasco J-1500 spectrometer equipped with a Peltier thermostated cell holder and Xe laser (lamp UXL-150S) in 0.5 mm dismountable quartz cells. Data was recorded at -11°C since a more intense signal was observed at this temperature compared to room temperature. For CD experiments at various temperatures see Figure S.5. The following parameters were used: 20 nm.min⁻¹ sweep rate, 0.05 nm data pitch, 1.0 nm bandwidth and 3 accumulations. The obtained signals were processed as follow: solvent and cell contribution was subtracted and the signals were smoothed (Savitzky-Golay method). For all samples, linear dichroism (LD) contribution was negligible ($\Delta LD < 0.005$ dOD). For more experimental details, see the Supporting Information.

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Keywords: Induced Circular Dichroism • Supramolecular polymers • Sergeants-and-soldiers principle • Gold complexes • Chirality transfer

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