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Supramolecular Photocatalyst for the Reduction of Au(III) to Au(I) and High-Turnover Generation of Gold Nanocrystals

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ABSTRACT: We report a photocatalyst composed of a diphenylanthracene core appended with two lipophilic thioether side chains that binds gold(III) chloride. Upon excitation using visible light, the AuIII ions are smoothly reduced to AuI which, in the presence of water, lead to the formation of crystalline gold nanoparticles of 20−50 nm diameter that are devoid of sulfur containing capping agents. Ultrafast transient absorption spectroscopy shows that the anthracene excited state is quenched with a rate k = 3.5 × 1010 s−1, assigned to intramolecular energy transfer to the bound gold ions, which then oxidizes the solvent to produce an intermediate low valency gold(I) species. In the absence of water, the latter is stable and can be used as a homogeneous AuI catalyst. When employed in a biphasic reactor, the photocatalyst shows average turnover numbers of 150 atoms of AuIII reduced to AuI per molecule of photocatalyst.

KEYWORDS: gold, nanoparticle, photocatalyst, homogenous catalysis, diphenylanthracene

1. INTRODUCTION

Supramolecular photocatalysts combine a molecular recognition motif with a photosensitizer designed to absorb light and promote a chemical transformation upon photoinduced electron or energy transfer process.1,2 Several such systems have been explored toward cycloaddition reactions, isomerization, and free radical transformations.3 In some cases, it has been possible to achieve turnovers greater than unity and mimic enzymatic behavior by combining hydrogen bonding interactions with photosensitizers for the oxidation of alcohols6 or for catalyzing intramolecular cyclization.7−10 The design of supramolecular photocatalysts has so far focused on the trans formation of organic molecules as they can readily combine a reaction center and a molecular recognition motif within a single species. In contrast, the design of supramolecular photocatalysts for the formation of inorganic species remains undocumented despite the potential of using light for smoothly preparing metal based catalytic intermediates or metal frameworks11 endowed with novel properties.

The photoinduced reduction of AuCl3 by triplet benzophenone was recently investigated in detail by the group of Scaiano and shown to proceed via a diffusion limited photoinduced electron transfer to generate Au nanoparticles (AuNP) and benzophenone oxidation products.12 We reasoned that a photosensitizer might be able to drive the photoreduction of a metal ion such as AuIII either by pumping electrons from the solvent to the gold ions, or by exciting the gold ions via an energy transfer mechanism. Such a system would be very useful for providing a photochemical route toward low valent Au species using long wavelength light that is not absorbed by common small organic molecules, as well as providing an example of the use of an organic photocatalyst for the generation of an inorganic material. Based on this, we designed a supramolecular photocatalyst containing a diphenylanthracene chromophore appended with two metal binding thioether side chains as such systems can promote strong interactions between the photoactive moiety and the metal ions.13 The thioether side chains are very lipophilic and render the gold−photocatalyst assembly soluble in organic solvents, thus allowing its selective photo excitation while preventing background irradiation of nonbound AuIII that remains in the aqueous phase. We show that the system can be readily steered toward either the production of a homogeneous AuI catalyst that can be directly used in organic synthesis, or toward the formation of uncapped gold nanocrystals. The latter can be produced in large quantities through the use of a recirculating reactor in which the catalyst reaches up to 170 catalytic cycles. Such turnover numbers are unprecedented for a supramolecular photocatalyst and demonstrate that photocatalytic generation of an inorganic material by an organic catalyst can be highly efficient. The reaction mechanism was elucidated by a combination of ultrafast absorption spectroscopy, product analysis, and dynamic 1H NMR spectroscopy.
2. EXPERIMENTAL SECTION

2.1. General Protocols. Reaction quantum yield measurements were measured at low conversion using monochromatic radiation from a medium pressure Xe–Hg lamp equipped with a monochromator. The samples (aerated) possessed absorbance ≥ 2 at the excitation wavelength and were stirred throughout the irradiation. Ferrioxalate actinometry was used to determine the photon flux (using $\Phi_{Fe^{III}} \rightarrow Fe^{II} = 1.20$ and 1.13 at 313 and 380 nm, respectively) and the Au concentration was determined spectrophotometrically. Fluorescence quantum yields were determined by comparison to a secondary standard (quinone sulfate in 2 N H$_2$SO$_4$, $\Phi_F = 0.54$).

2.2. Preparation of Gold(III) and Gold(I) Complexes. Complex 1:2AuCl$_3$ was obtained by two methods that gave identical results: (i) dissolution of solid HAuCl$_4$ or KAuCl$_4$ into a solution of 1 (toluene or dichloromethane) or (ii) extraction of AuCl$_3$ from an aqueous solution of HAuCl$_4$ by a solution of 1 in toluene or dichloromethane. The binding of AuCl$_3$ by 1 was followed spectroscopically by monitoring the absorption of Au(III) at 330 nm, and the complexes were characterized using mass spectrometry (FD$^\dagger$). Complex 1:2AuCl$_3$ was obtained by irradiating a solution of 1:2AuCl$_3$ in toluene (0.1–1 mM), at 20 °C, using a TLC lamp (365 nm, 6W) or LED (400 nm, 10W), for 15–30 min.

2.2. Preparation of AuNP. A solution of 1:2AuCl$_3$ in dichloromethane or toluene (0.1 to 1 mM, 10 mL) was prepared in a centrifugation tube (50 mL). Water (10 mL) was added and the biphasic system was agitated on an orbital stirring table at 300 rpm while irradiated using a TLC lamp (365 nm, 6W) or a LED (400 nm, 10W) for 15 min. The reaction mixture was then centrifuged at 1500 rpm for 15 min and the aqueous phase, containing gold nanoparticles, was collected.

2.3. Photoreduction Reactor and Calculation of Turnover Number. To estimate the maximum number of turnover cycles that can be performed by 1, the recirculating reactor described in Figure 9 was loaded with 1 (initial concentration = 15 μM, Vol = 40 mL) and an excess of HAuCl$_4$ (initial concentration = 6 mM, Vol = 50 mL). The absorption spectrum of the aqueous phase was monitored at $t = 0$ and 15 h (end of conversion) by withdrawing an aliquot (100 μL) and diluting it in 2 mL H$_2$O. Using the extinction coefficient of the HAuCl$_4$ solution at 290 nm, the concentration of Au$^{III}$ remaining in solution can be determined. The turnover number is calculated in terms of moles of consumed Au$^{III}$ ions per moles of 1 consumed.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Au Complex. The photocatalyst used in this study is easily prepared in three steps from commercially available reagents (72% overall yield). All spectroscopic analyses are consistent with the structures shown in Scheme 1. As expected for diphenylanthracene derivatives, 1 is highly fluorescent in nonpolar organic solvents ($\Phi_F = 0.96$, $\tau = 7.5$ ns in toluene, $\lambda_{em} = 365$ nm), although photooxidation of the thioether groups occurs in solvents of moderate polarity via a known photoinduced electron transfer mechanism.

The thioethers in 1 are designed to bind two AuCl$_3$ and maintain them in the vicinity of the anthracene chromophore.

With this in mind, flexible ethylene glycol subunits were introduced in the linker to alleviate unfavorable gauche interaction associated with folding of the chain. To examine compound 1’s ability to bind AuCl$_3$, a solution of 1 in dichloromethane or toluene was placed in contact with an aqueous solution of HAuCl$_4$ or with solid AuCl$_3$. Upon gentle shaking, the yellow color of the Au$^{III}$ was transferred to the organic phase which became nonfluorescent. Complexation can be readily followed by UV–vis or emission spectroscopy (Figure 1). In all cases, whether by titration of 1 by the Au$^{III}$ salt or by measuring the amount of Au$^{III}$ salt lost from the aqueous phase upon incremental addition of 1, the stoichiometry was found to be 1:2 (1: AuCl$_3$).

In agreement with the formation of a 1:2 complex, mass spectrometric analysis of the organic phase following extraction
of AuCl₃ by I evidenced the presence of a molecular ion with m/z = 1630 Da corresponding to a species with the formula I·2AuCl₃ (Figure 2A). Irradiation of anhydrous I·2AuCl₃ solutions in toluene or dichloromethane (aerated or Ar saturated) at 365 or 400 nm, where the diphenylanthracene chromophores absorb, results in the rapid reduction of the AuIII into AuI, as evidenced by the discoloration of the solution and by MS analysis of the photolyzed solution which now only shows signals corresponding to the dissociation of I·2AuCl₃ (Figure 2B).

The solid state structure of the I·2AuCl₃ complex is not currently known, as it is a waxy solid that is not amenable to X-ray diffraction analysis. However, binding of AuCl₃ is likely to occur at the sulfur positions in I as generally observed for thioethers (Scheme 1). Diffusion ordered NMR spectroscopy (DOSY) was used to obtain information regarding the diffusion constant of I and the I·2AuCl₃ complex in dichloromethane (Figure 3). The latter gives a narrow distribution of diffusional rates centered around the value of 5.44 × 10⁻¹⁰ m²/s, compared to a diffusion constant of 1.75 × 10⁻⁹ m²/s for I under the same conditions. In the case of the I·2AuCl₃ complex, the observed diffusion constant corresponds to a calculated Stokes radius of Rₛ = 8.9 Å (Vₛ = 2950 Å³), which is in good agreement with the solvent excluded volume calculated for a compact structure using a PM3 semiempirical model (3250 Å³). The observation that the ¹H NMR spectrum of the I·2AuCl₃ complex is sharp, and that its diffusion coefficient is only reduced by one half with respect to I strongly argues against the formation of coordination polymer networks, which would be expected to exhibit broadened NMR signals and considerably reduced diffusional constants.

The formation of coordination polymers or aggregates would be expected to greatly influence the reduction of Au species by accelerating the formation of Au clusters and seeding. To further verify that binding to AuCl₃ did not induce aggregation of the complex in solution, experiments using high field (800 MHz) and variable temperature ¹H NMR were undertaken. At room temperature, the ¹H NMR spectrum of the I·2AuCl₃ complex in CD₂Cl₂ is sharp, with the exception of the aromatic protons of the diphenylanthracene core which are somewhat broadened (see Figure 4A and B). No broadening of the dodecyl or ethylene glycol chains is observed, suggesting that the complex is not aggregated in solution and that the aromatic core experiences slow interconversion between different environments. Hindered rotation of the diphenylanthracene moiety in I would be expected upon complexation of AuIII if the complex adopts a compact conformation as suggested by the results from DOSY. In agreement with this, we find that these signals sharpen upon lowering the temperature to 203 K (Figure 4C). From the coalescence temperature of the aromatic protons at 7.4 ppm, an activation barrier for equilibration of ca. 60 kJ/mol is calculated. This behavior is contrary to that expected for aggregation, which is instead favored at low temperatures and generally induces increased broadening of NMR signals.

### 3.2. Photoreduction of AuII and Catalytic Behavior of Au Complex

As mentioned above, irradiation of the I·2AuCl₃ complex in toluene or dichloromethane (λ ≥ 365 nm) in the absence of water rapidly leads to the formation of AuCl species as expected for the photoreduction of the AuCl salt. The efficiency of the reduction process can be monitored from the disappearance of the absorption band associated with AuIII bound to I upon selective irradiation of the anthracene chromophore. Irradiation at 380 nm of aerated toluene or dichloromethane solutions of I·2AuCl₃ led to the rapid disappearance of the absorption band of AuIII with quantum yields of 0.07 and 0.06, respectively. Because AuII salts possess similar electronic transitions as AuIII salts, we believe that these values correspond to the formation of AuI species,
which are transparent in the visible and near UV region of the spectrum. In this case, the observed quantum yields represent the overall reduction process of AuIII to AuI, which would be two consecutive reduction steps. Thus, assuming that each of the two photoreduction steps leading to AuI from AuII occurs with similar efficiency, the overall quantum efficiency of each photoreduction process would be 0.26. This indicates that the sequential energy transfer/solvent oxidation process is efficient and comparable to that observed by reductive photoinduced electron transfer to AuII from an excited donor. Energy wasting processes, possibly through spin exchange quenching of the anthracene excited state and vibronic relaxation, therefore amount to a quantum yield of 0.74.

The photolyzed solution can be directly used to catalyze organic reactions promoted by AuI. To demonstrate this, we investigated the intramolecular ring closure of t butyl propargylamide using photolyzed and nonphotolyzed solutions of 1-2AuCl. It is known that the reaction is catalyzed by AuIII species to form the corresponding oxazole, whereas the use of an AuI catalyst leads to the formation of the methylene dihydrooxazole. As expected from the proposed photoreduction of AuIII to AuI, the use of the irradiated 1-2AuCl solution led to the rapid and exclusive formation of the dihydrooxazole, whereas use of nonirradiated 1-2AuCl solution led to formation of the oxazole (Scheme 2). Thus, the supramolecular complex behaves as a light sensitive catalyst in which it is possible to control the nature of the catalytic species (AuI or AuIII) simply by irradiation with visible light.

### Scheme 2. Catalytic Activity of Homogeneous 1-2AuCl and 1-2AuCl Formed by Irradiation on the Intramolecular Ring Closure of t Butyl Propargylamide

![Scheme 2](image)

**Figure 4.** High field 1H NMR (800 MHz, CD2Cl2) of 1 (A) and 1-2AuCl (B). The latter exhibits broadening of the signals of the aromatic protons, but not of the signals associated with the alkyl or ethylene glycol chains. This is interpreted as resulting from slow conformational interconversion of the anthracene moiety upon formation of the Au complex in agreement with VT NMR (600 MHz, CD2Cl2) which shows sharpening of the signals at low temperature C.

3.3. Photogeneration of Au Nanocrystals. In the absence of water, the 1-2AuCl complex is relatively stable and undergoes slow dismutation over several days to form AuI and AuCl3. In contrast, the presence of water promotes the formation of gold nanoparticles (AuNP), which is complete in 45–60 min in water/toluene or occurs during irradiation if water/dichloromethane is used as a reaction medium. The appearance of a ruby red coloration of the aqueous phase (λmax = 535 nm) observed is typical of the absorption from the plasmon resonance of AuNP that are ca. 30 nm in size. Transmission electron microscopy (TEM) images of the particles suspended in the aqueous phase are shown in Figure 5. They unambiguously identify the nanoparticles as crystalline AuNP of dimensions that are between 20 and 50 nm. Further inspection shows that they are formed by the agglomeration along crystal growth axes of smaller (ca. 5 nm) AuNP that are also crystalline.

The process leading to the formation of AuNP is broadly similar to that previously observed for the photoreduction of aqueous solutions of Au complexes. However, we observe that in this case the Au0 atoms formed undergo nucleation and eventually migrate to the aqueous phase due to the hydrophilic nature of pristine gold, thereby releasing the photocatalyst which remains in the organic phase. In support of this, X ray photoelectron spectroscopy (XPS) analysis of the AuNP reveals the presence of chlorine atoms along with carbon and oxygen, whereas the amount of sulfur atoms is below the detection limit (Figures 6). This result shows that 1 is not extracted into the aqueous phase along with the nanoparticles, which are instead stabilized by chloride anions and traces of organic molecules. The XPS analysis also revealed the presence of cationic Au species, which may also contribute to the stabilization
of the AuNP and provide further opportunities for applications in catalysis.28

3.4. Mechanistic Investigation. Several pathways have been reported for the photoreduction of AuIII salts into AuNP, the most common of which being the use of pulse radiolysis or photoinduced fragmentation of a suitable precursor to generate a chemical reductant.29,30 Direct irradiation of AuIII in the presence of ethylene glycol and a capping agent using broad wavelength UV light (250–400 nm) yields small (7 nm diameter) spherical AuNP through a mechanism involving glycol oxidation.31 Uncapped AuNP can be obtained by reduction of HAgCl by photogenerated ketyl radicals in water,24 direct excitation of AuCl− in the presence of a reductant,25 or via an electron transfer process from excited benzophenone.12 However, all of these mechanisms result in the loss of the absorbing chromophore, which therefore does not exhibit catalytic activity. In contrast, we find that when toluene is used as the organic phase, there is no degradation of I and that the toluene solution of I can be isolated and reused to prepare another batch of AuNP. This cycle was repeated five times with no apparent loss of efficiency, confirming that I acts as a photocatalyst in contrast to previously reported photoreductants.

The mechanism by which AuCl3 is reduced to AuI or to Au0 involves initial excitation of the diphenylanthracene chromophore as this absorbs the majority of the incident radiation at λ = 365 nm. Oxidative electron transfer quenching of the diphenylanthracene excited state by AuCl3 would be expected to proceed through a single electron transfer to generate AuIIICl3 and is calculated to be thermodynamically favorable by ΔETG0 = −0.5 eV using eq 1,12

$$\Delta_{ET}G^0 = N_A \left[ e \left( E_0(D^{+\bullet\bullet}/D) - E_0(A/A^{\bullet\bullet}) \right) + w(D^{+\bullet\bullet}A^{\bullet\bullet}) \right] - \Delta E_{00} \tag{1}$$

where $N_A$ is the Avogadro constant, $e$ is the elementary charge, $\Delta E_{00}$ is the energy level of the singlet excited state of I (3.08 eV), and $E_0(D^{+\bullet\bullet}/D)$ and $E_0(A/A^{\bullet\bullet})$ refer to the oxidation and reduction potential of I (+1.46 V vs V NHE) and AuIIICl3, respectively. The reduction potential of the AuIII/AuI couple was bracketed between +0.35 and +0.71 V by Scaino and coworkers,12 and a value of +0.6 V vs V NHE as estimated by Gachard et al. from pulse radiolysis experiments33 was used in the calculation. The Coulombic term was calculated according to $w(D^{+\bullet\bullet}A^{\bullet\bullet}) = 2e^2/(4\pi\varepsilon_0\varepsilon_r\sigma)$, where $\varepsilon_0$ and $\varepsilon_r$ are the vacuum and relative electric permittivity, respectively, and $\sigma$ is the separation between D+ and A− (0.7 nm).

Photoinduced electron transfer in I-2AuCl3 would be expected to be fast as it is intramolecular and not limited by the diffusion of the reactants. Femtosecond time resolved transient absorption spectroscopy was therefore used to identify the initially formed excited state as well as the primary photoinduced processes upon light absorption. In the case of electron transfer quenching, the ensuing diphenylanthracene radical cation possesses a characteristic spectral signature at 500–600 nm that is easily identified.34 Upon pulsed excitation ($\lambda_{ex} = 380$ nm, 40 fs), the absorption spectrum of the $S_1$ state of the diphenylanthracene chromophore is clearly visible ($\lambda_{max} = 560$ nm, Figure 7), thereby excluding direct population of the anthracene triplet state owing to strong spin–orbit coupling induced by the Au atoms. The anthracene $S_1$ signal decreases rapidly with a time constant of 27 ps (in either toluene or dichloromethane), from which a rate constant for intramolecular quenching of the singlet excited state of I by the bound gold ions $k_q = 3.7 \times 10^{10}$ s−1 can be determined. However, no signal corresponding to the absorption of the radical cation of I or of the diphenylanthracene $T_1$ state can be detected, and the repopulation of the ground state was found to occur on the same time scale as the depopulation of the $S_1$ excited state.35 This implies that either the ensuing reaction of the diphenylanthracene excited state is too fast to be monitored by transient absorption spectroscopy, or it involves a process that is too slow to be probed in the femtosecond range.
AuIII and AuI, and the process is repeated (not shown, see text). In the presence of water, nucleation of the Au0 atoms leads to the formation of AuNP which migrate to the aqueous phase and release AuII into organic phase to continue the reduction cycle.

Intramolecular energy transfer from the excited diphenylanthracene chromophore to AuIII could occur via a spin exchange mechanism. The former requires orbital overlap between the donor and acceptor which is not apparent from the 1H NMR or electronic absorption spectrum of the complex. In the case of FRET, the distance separating the donor-acceptor pair can be calculated from the observed energy transfer rate and the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor using eq 2:

\[
  k_{\text{EnT}} = \frac{1}{\tau_D} \left( \frac{R_0}{r} \right)^6
\]

where \( \tau_D \) is the lifetime of the excited donor and \( R_0 \) is the Förster radius (calculated from the spectral overlap to be 2.3). From eq 2, an average Au--anthracene distance of 9 Å is calculated for quenching in the 1-2AuCl3 complex, which is consistent with an intramolecular energy transfer process.

Comparison of dichloromethane and toluene as an organic medium reveals important differences in behavior. When dichloromethane is used, MS and NMR analysis of the organic phase after formation of the AuNP show that I has decomposed, principally by cleavage of the chains in the benzylic position and \( \alpha \) to the thioethers. In contrast, when toluene is used as an organic phase, I does not decompose and the presence of toluene byproducts (benzyl chloride, benzaldehyde, chlorotoluene) is detected instead. These may be formed through a mechanism involving oxidation of toluene by photoexcited AuIII or through the release of chloride radicals from the 1-2AuCl3 complex analogously to the photoejection of Cl- from AuCl4- as described by McGillivray et al.

From the experimental observations, a reaction mechanism can be proposed for the photoreduction of AuIII into AuI, which in the presence of water continues to the reduction of AuI into AuNP (Figure 8). Catalyst I binds two AuCl3 molecules to form a 1-2AuCl3 complex that is soluble in the organic phase. Upon excitation at 400 nm, the anthracene chromophore is excited preferentially and ultrafast energy transfer populates the AuIII excited state which is a strong photooxidant. If the reaction is conducted in toluene, the excited AuIII complex oxidizes the solvent to produce AuII ions and toluene oxidation byproducts. If toluene is replaced by dichloromethane, then the excited AuIII complex oxidizes I, eventually leading to its decomposition. It is commonly assumed that AuIII species formed during the reduction of AuIII ions undergo dismutation to form AuI and AuIV. This is indeed observed if the irradiation is stopped after 1–2 min, but the process is relatively slow as the concentrations involved are low (several hours). This is not entirely compatible with the rapid transformation of AuIII that is observed upon continued irradiation and it is possible that a light induced process for the consumption of AuIII is also operating in competition with dismutation of AuII. Because it is known that...
Au^{III} species absorb more intensely and at longer wavelengths than the corresponding Au^{II} complexes,\(^{20}\) it is possible that energy transfer to the Au^{III} complex from the diphenylanthracene \(S_2\) state is as fast or faster than energy transfer to the Au^{III} species. The excited Au^{II*} ion would once again oxidize the solvent to generate Au^{I}. The latter does not absorb in the visible range,\(^{20}\) thereby stopping the energy transfer quenching of the \(S_1(1)\) excited state.

3.5. Catalytic Turnover. In order to calculate the maximum turnover cycles of 1 in toluene, we constructed a recirculating reactor that allows the selective excitation of the organic phase while protecting the aqueous phase from light to avoid possible background photoreduction of excess Au^{III} (Figure 9). The reactor is composed of an extractor in which the catalyst in the toluene organic phase is exposed to a large excess of HAuCl\(_4\) contained in the aqueous phase. The supernatant organic solution is pumped through a glass tube that is exposed to two 10 W 400 nm LED sources and then circulated back into the aqueous subphase in which an excess of HAuCl\(_4\) is present. The amount of Au^{III} present in the aqueous phase is determined spectroscopically at various intervals.

Figure 9. Recirculating reactor constructed to determine the maximum turnover cycles attainable by 1. The biphasic reactor draws the toluene solution of the I-2AuCl\(_3\) complex from the supernatant, which is then sent to a photoreactor enclosure composed of glass tubing that is irradiated by two 400 nm 10 W LED sources. The irradiated solution is then pumped back into the reactor through a glass frit located in the aqueous subphase in which an excess of HAuCl\(_4\) is present. The amount of Au^{III} present in the aqueous phase is determined spectroscopically at various intervals.

Table 1. Initial and Final Au^{III} Concentrations from Five Runs of Au^{III} Reduction Using the Recirculating Reactor Shown in Figure 9\(^a\)

| run | t (h) | 1 | 2 | 3 | 4 | 5 |
|-----|------|---|---|---|---|---|
| OD (287 nm) | 0.797 | 0.592 | 0.821 | 0.567 | 0.788 | 0.521 | 0.745 | 0.447 | 0.787 | 0.581 |
| [Au^{III}]\(^b\) (mM) | 5.58 | 3.98 | 5.75 | 3.97 | 5.52 | 3.65 | 5.21 | 3.13 | 5.51 | 4.06 |
| TON | 133 | 148 | 156 | 174 | 121 |

\(^a\)\(V_{aq} = 50\) mL, \([1] = 15\) \(\mu\)M, \(V_{org} = 40\) mL. \(^b\)Determined using \(\epsilon(HAuCl_4) = 3150\) M\(^{-1}\).cm\(^{-1}\).
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