Charge-Transfer Mechanisms between Gold Clusters

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Electron-transfer processes in complex chemistry are usually described by Taube's "outer sphere" and "inner sphere" mechanisms. A behaviour related to these electron-transfer mechanisms in complex chemistry can be observed for charge-transfer transport between ligand protected Au_{55} nanoclusters. A linear dependence between cluster-cluster distance and activation energy for electron transfer is observed if a noncovalent linkage exists; this interaction is independent of the distance in covalently linked clusters. Instead, the activation energy depends on the electronic nature of the linking molecules. The dithiols 1,5-dithionaphthaline (**1**), 4,4′-thiobis(benzenethiol) (**2**), and 2,8-dithio-6-hydroxypurine (**3**) have been used as bifunctional covalent linkers either in their monomeric form (**2**) or, in the presence of air, dimerized via S–S bonds (**1**, **2**, **3**), causing an increase in the distance between the clusters and leading to the cluster networks **4**–**7**. Noncovalent cluster networks are formed either by pellets of clusters with monodentate ligands in **8** and **11**, linked only by van der Waals forces, or by using bifunctional spacers that interact with the clusters by ion attractions (**9**, **10**).
A study of the activation energies clearly indicates that in the case of noncovalently organized nanoparticles only the cluster spacing is of relevance, even if conjugated π-systems like in **10** are used. This behaviour corresponds to an outer-sphere mechanism. On the contrary, for covalently linked clusters the distances between them does not play a visible role. The activation energies all lie below those of the noncovalent examples, and a relation between cluster-cluster distance and activation energy is not obvious. In those cases the relationship suggests an inner-sphere mechanism where the transport properties of the spacer play a decisive role.
These findings possibly help to explain contradictory reports on the conductivity behaviour of organic molecules.
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Introduction

The study of the electric properties of nanosized materials is a rapidly emerging field of great fundamental and practical interest owing to their potential as building blocks in future nanoelectronic devices. Much of the recent work is therefore driven by prospective applications in nanoelectronics, nonlinear optics, sensors etc. The charge-transfer properties of individual particles,[1−3] monolayers,[4−6] multilayers,[7,8] as well as of three-dimensional structures[9−11] have been investigated. Generally, it was found that the electrical conductivity depends on the size of the particles[12] and on the distance between them.[13] Whereas particles with diameters larger than about 2 nm were suggested to be used for the fabrication of nanowires to connect electrical circuit elements,[14] particles smaller than 2 nm are promising candidates for room-temperature single electron transistors[15] since the rate-limiting step of the electron-transfer process is the charging of the particles. Therefore, charge transport is connected with a relatively high activation energy.

In order to vary the activation energy for electron transfer between nanoparticles many different ligand molecules or interconnecting spacers have been applied. Among these are thiols and dithiols,[7,16−18] dicyanides,[5] phosphanes,[9,10,15] and other molecules with or without conjugated π-systems.[5,19] There is, however, no agreement among different authors whether and/or in which way the chemical nature of the spacers influences the conduction properties of the nanoparticle arrangement[4,5] or not.[13,15,20] It has been shown that the resistance of an adsorbed monolayer on a surface, measured by STM, depends on the nature of the end groups of the adsorbed molecules.[21] This effect was interpreted by the conduction through the highest occupied molecular orbitals (HOMOs) or the lowest unoccupied states (LUMOs).

On the other hand we found that the activation energy for charge transport in three-dimensional cluster arrangements depends simply on the cluster spacing rather than on the chemical nature of the molecules between them.[22] This is reflected by an almost linear dependence of the activation energy on the cluster spacing that is observed provided that

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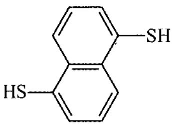
the cluster linkage results from ionic coupling instead of a covalent linkage. A simple approach based on the Landauer formula, which allows a first-order estimate of the resistance of the linking molecules, leads to the conclusion that the charge transport between clusters via organic molecules (ligands/spacers) involves tunnelling rather than propagation.[20]

Results and Discussion

In this paper we report on the synthesis and electrical characterisation of different types of covalently crosslinked Au_{55} clusters in order to compare the charge-transfer properties with those of previously described noncovalently organized systems. For that purpose we used three different dithiols, since sulfur−gold bonds are of a strongly covalent character and dithiol-protected clusters can be three-dimensionally linked through direct Au-dithiol-Au bonds or S−S bonds formed by smooth oxidation of the second SH groups.

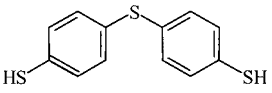
As dithiols we used

1,5-dithionaphthaline (DNP)



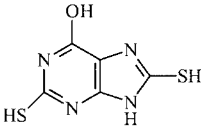
1

4,4'-thiobis(benzenethiol (TBBT)



2

and 2,8-thio-6-hydroxypurine (purine)



3

The process aimed is illustrated schematically in Figure 1.

The formation of the dithiol-stabilized gold clusters results from ligand-transfer reactions and has been performed previously with various other thiol ligands.[7,23,24] As shown in Figure 1, the first step should represent the formation of individual thiol-stabilized clusters (A) which have not been isolated. Afterwards, two further reactions can take place: in the absence of air, the terminal thiols can interact directly with other clusters (B) (due to the high steric hindrance, this exchange can need several weeks), whereas in the presence of air, fast oxidation of the free SH groups to S−S disulfide bridges occurs, crosslinking the clusters (C). This process can be followed by the formation of brown precipitates, consisting of three-dimensionally linked cluster-dithiol hybrid materials, and residual colourless solutions.

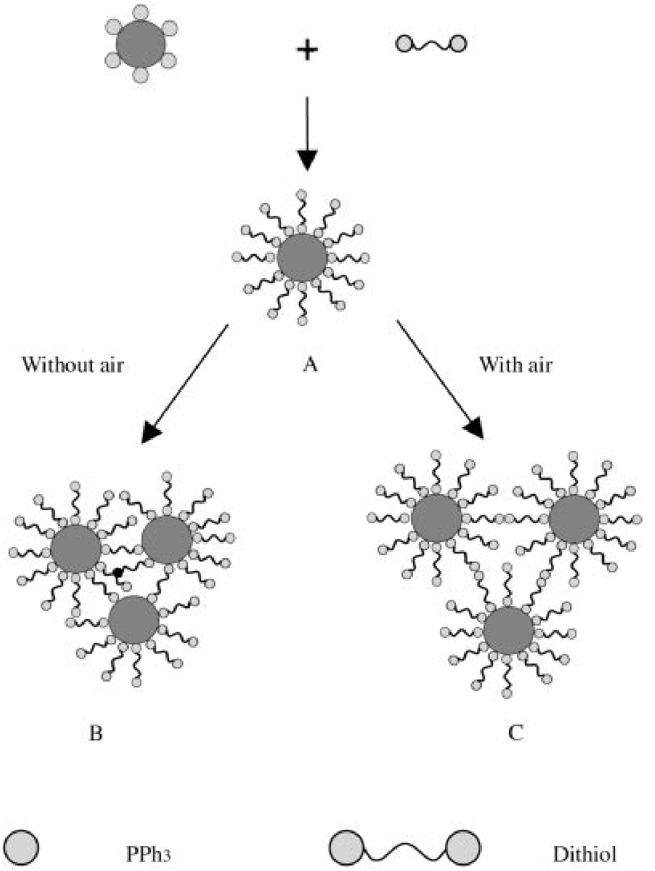


Figure 1. Schematic representation of the cross-linkage of Au_{55} clusters with dithiols (A); without air, aggregates of type B are formed, whereas in the presence of air aggregates C, with S−S bridges, result

Under a nitrogen atmosphere, well-ordered arrangements of Au_{55} clusters, directly linked by the spacer molecule **2** through formation of Au−S bonds, were observed (**4**, Figure 2, top). In air, various assemblies of clusters were formed (**6**, Figure 2, middle). These clusters do not adopt a specific ordering, but a regular average distance of 2.3 nm between two adjacent particles attests to the presence of a disulfide bridge. In contrast to **4**, which took about two weeks to form and precipitate, the formation of **6** was finished after two hours so no higher organization is possible. This lack of organisation can be explained by the fact that the spacer molecules used are long and flexible enough to fold during the experiments modifying the inter-particle distance. The number of spacer molecules present around one Au_{55} cluster depends on the ligands used. Because of the nature of the product (insoluble polymer), the elemental analysis does not allow the determination of the exact stoichiometry of the compounds, but only an estimation concerning the number of linkers present around each cluster. The results are the following:
entity 4: $Au_{55}[TBBT]_{22/2}$; entity 5: $Au_{55}[purine]_{16}$; entity 6: $Au_{55}[TBBT]_{14}$; entity 7: $Au_{55}[DNP]_{18}$.

As a blank, one drop of a solution of gold clusters was deposited onto a TEM grid (Figure 2, bottom). In this case, no special kind of organisation of the gold particles was observed. For the electrical measurements the washed and

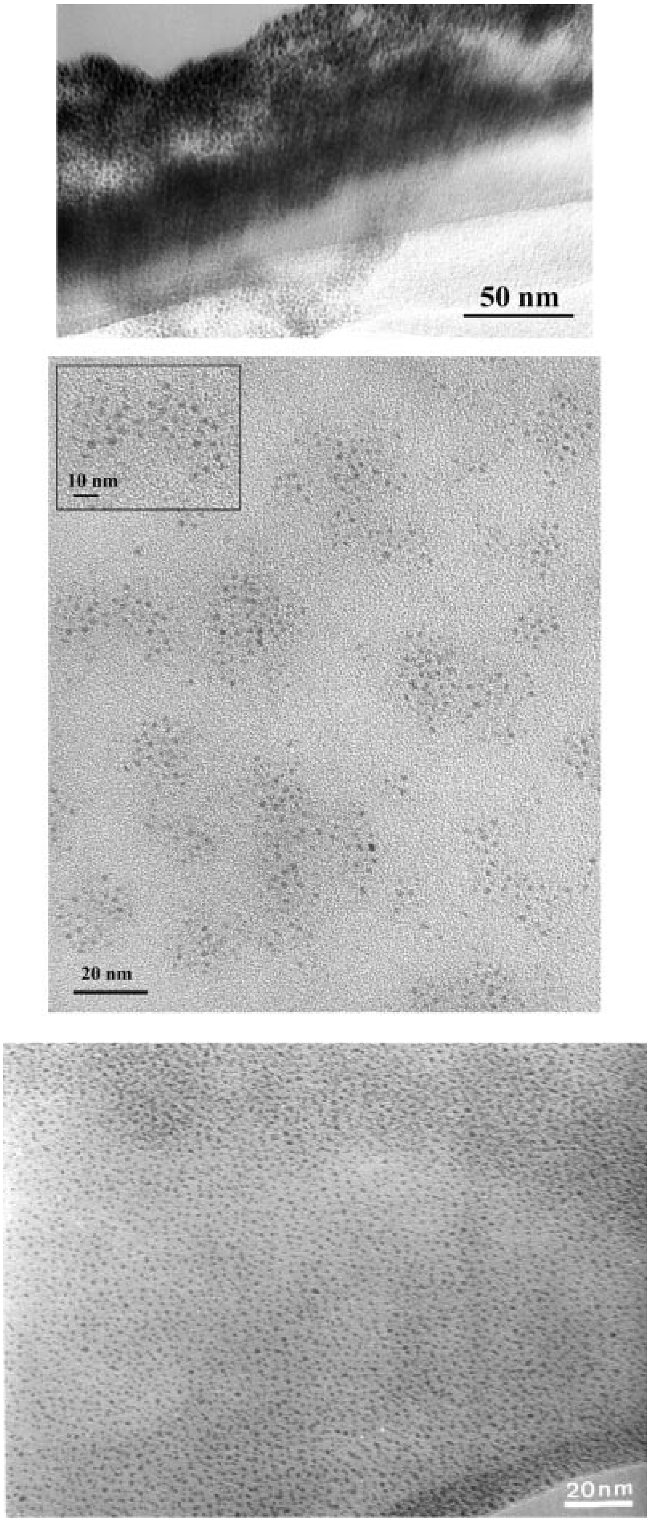


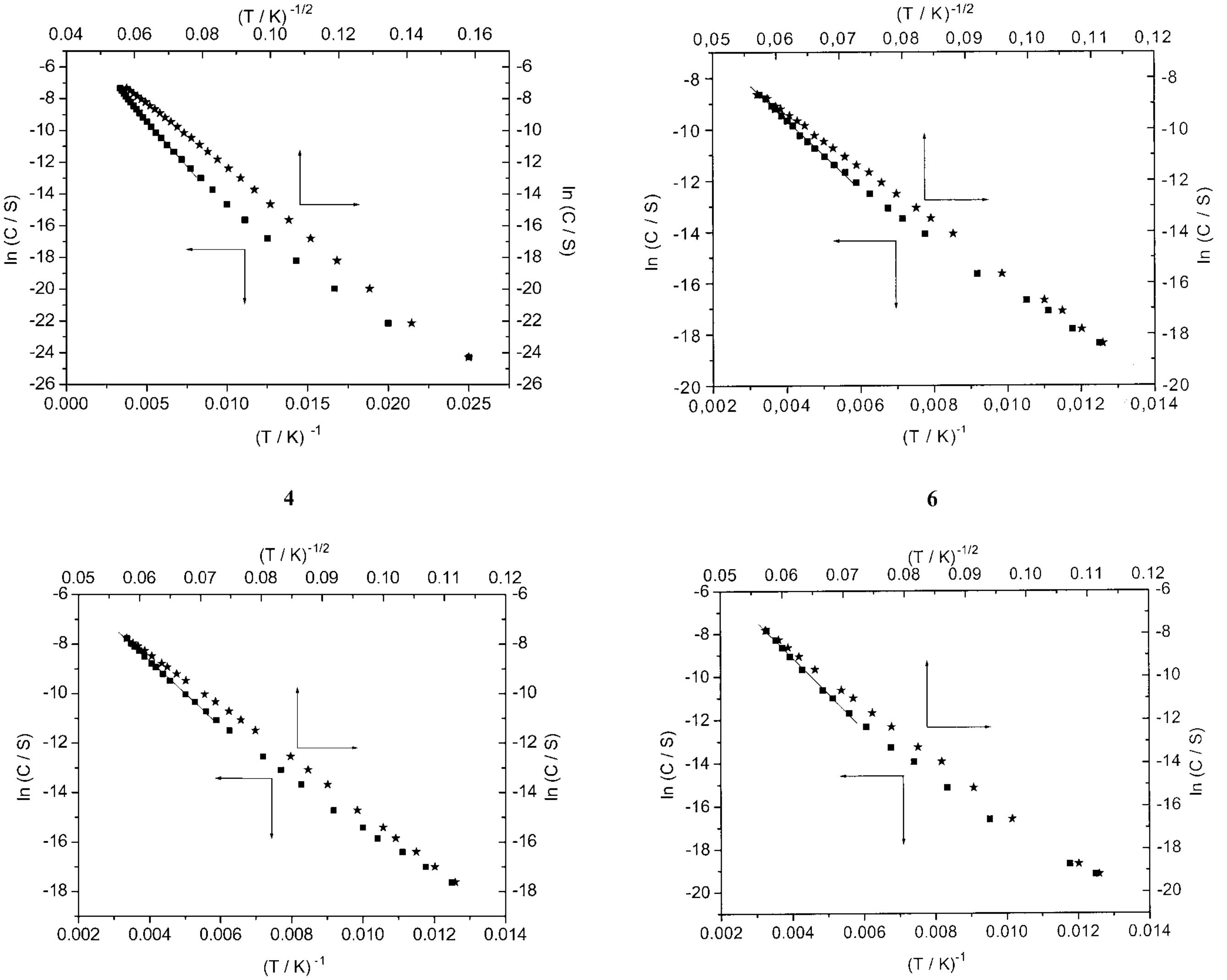
Figure 2. (top): TEM image of an ordered arrangement of $[Au_{55}Cl_6(PPh_3)_{12}]$ clusters linked by the spacer molecule **2** without oxygen (sample **4**); (middle): TEM image of $[Au_{55}Cl_6(PPh_3)_{12}]$ clusters linked by the spacer molecules **2** in the presence of air (sample **6**); the insert shows the magnified aggregate below; (bottom): TEM image of nonlinked $[Au_{55}Cl_6(PPh_3)_{12}]$ clusters

carefully dried precipitates were pressed into pellets and contacted on the top and bottom with silver paint. The activation energies were determined by temperature-dependent conductivity measurements. The temperature dependence shows simply activated behaviour for a temperature range between 200 K and 300 K. In this temperature range the charge transport is due to thermally activated electron exchange between neighbouring clusters. The corresponding activation energy E_a i.e. the charging energy of the particles in the three-dimensional arrangement, is determined by the respective particle size and spacing. Thus, E_a represents the charge disproportionation energy, which needs to be overcome to create mobile charge carriers.[25] Below 200 K a transition from nearest neighbour exchange to variable range exchange is observed, leading to a temperature dependent activation energy. In these experiments E_a was determined between 200 K and 300 K by a regression line fit. Figure 3 contains the experimental curves of the investigated samples and Table 1 summarises these data together with the calculated cluster distances. In addition, the corresponding data for the non-covalently crosslinked clusters of our previous investigations[15,25,26] are included for comparison.

Figure 4 illustrates the data of Table 1. As already mentioned, in the case of noncovalently crosslinked Au_{55} clusters there is a linear relation (correlation coefficient: 0.992) between cluster-cluster distances and activation energies, indicating that only the distance between the nanoparticles determines the energy of the hopping processes. The chemical nature of the linking molecules obviously plays a minor role. This can be understood due to the fact that there is no direct electronic interaction between the clusters via either the stabilizing ligand molecules in a close packing in samples **8** and **11** (van der Waals attraction), or the crosslinking spacer molecules in **9** and **10** (ionic attraction between spacer and functional groups and outer ligand sphere). This is most visible in the case of the spacer in sample **10**, which comprises a conjugated π-system along its backbone and from which a molecular conducting behaviour might be expected. Instead, E_a also depends on its length, implying that propagation along the π-system is blocked by the ionic interconnection between spacer and ligand.

On the contrary, the dithiol spacers link the clusters directly by covalent bonds. The activation energies are characteristically lower and do not depend linearly on the cluster spacing. Although a direct relation between the molecule length, electron density, symmetry etc. and E_a could not be established, it is obvious that the chemical nature of these molecules, which differ considerably among each other, essentially affect the transition probability for electrons between the clusters. This suggests an electron-transport mechanism, where bonding and/or antibonding molecular orbitals of the linking molecules are involved in the conductivity process.

In a first-order approximation the difference between directly (covalent) and nondirectly (van der Waals, ionic) linked clusters can be compared with the mechanisms of classical redox processes, which have been divided into "outer sphere" and "inner sphere" mechanisms.[27−31] The inner-sphere mechanism of electron transfer is characterised



4

6

5

7

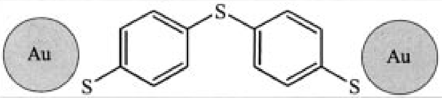
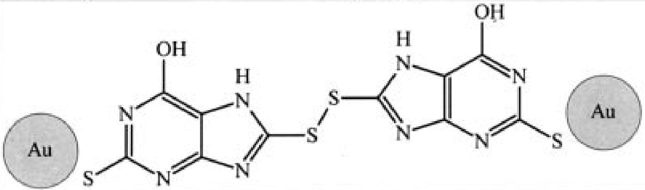
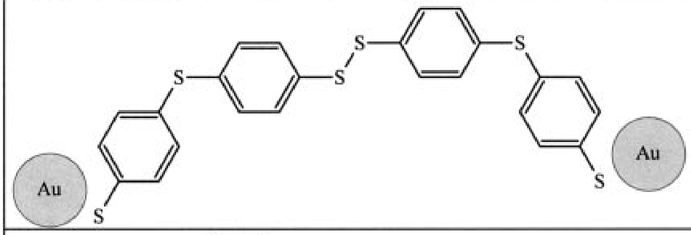
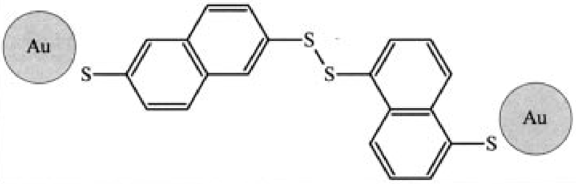
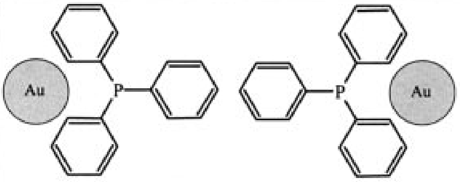
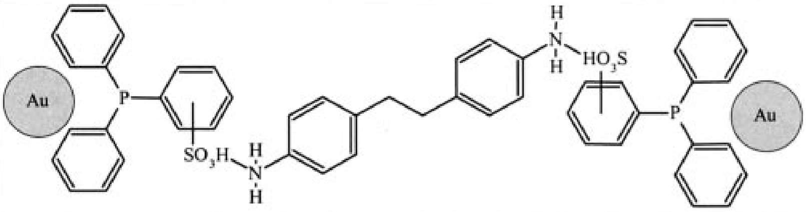
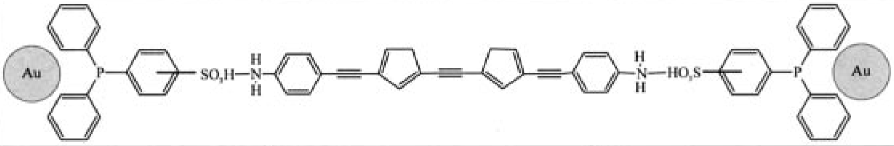
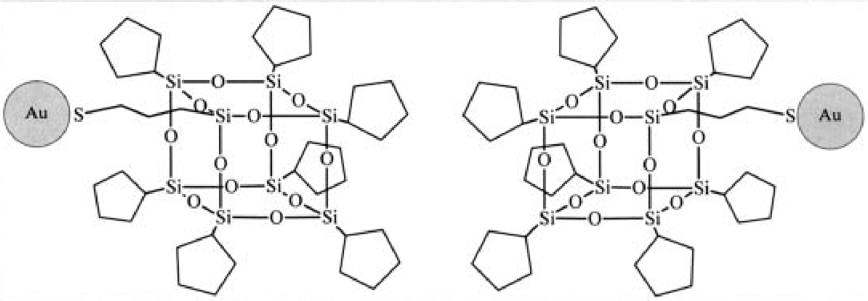
Figure 3. Experimental curves (temperature versus conductance) of **4**, **5**, **6**, and **7**

by the participation of a bridging ligand between the oxidizing and the reducing metal ion. In the outer-sphere process the coordinated metal ions simply touch each other via their coordination spheres, and the electron transfer has to occur through the ligand shell and probably involves a deformation of the coordination spheres. Electron transfer between clusters can indeed be compared with those redox processes. The initial step for the creation of free charge carriers is the charge disproportionation of two initially neutral clusters in the immediate vicinity. Thus, charged cluster pairs represent both reduced and oxidized species, and E_a corresponds to the inverse of the electron-transfer rate, which is essentially higher in redox pairs with direct coupling (inner-sphere mechanism).

Conclusion

We have shown that electron-transfer processes between Au_{55} clusters can occur in two different ways: compared with classical inner-sphere redox processes, noncovalently linking molecules simply act as spacers, independent of their chemical nature, and require activation energies that correspond only to their length. Covalently cluster-linking

Table 1. Activation energies and cluster-cluster distances of the covalently and the non-covalently organized systems

Covalently Linked			
Linking System		Distance [nm][a]	E_a [eV]
	**4**	1.1	0.095
	**5**	1.6	0.11
	**6**	2.3	0.12
	**7**	1.5	0.14
Noncovalently Linked			
Linking System		Distance [nm][a]	E_a [eV]
	**8**	0.7	0.16
	**9**	1.9	0.2
	**10**	2.8	0.23
	**11**	3.1	0.26

[a] The length of the molecules was determined using the program ACD-ChemSketch.

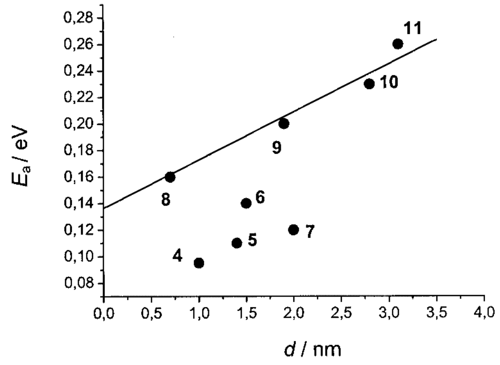


Figure 4. Activation energies versus cluster-cluster distances of the covalently (**4−7**) and the noncovalently (**8−11**) organized systems

species, possessing delocalised π-electrons, enable inter-cluster electron transfers by lower activation energies, depending on the electronic situation in the molecule, not only on their lateral extension. These results give a new insight into the charge-transport mechanism between nanoparticles, and long and controversial questions concerning the nature of this transport − whether it involves propagation via the organic molecules or whether it predominantly involves tunnelling − can now be considered as at least partially to be answered.

Experimental Section

General: 4,4′-Thiobis(benzenethiol) (**2**) and 2,8-dimercapto-6-hydroxypurine (**3**) were purchased from Aldrich (98% purity) and from Avocado (98% purity), respectively. 1,5-Dithionaphthalene (**1**) was synthesised from 1,5-naphthalenedisulfonic acid sodium salt hydrate (Aldrich, 95% purity) following described synthetic procedures.[32,33] [$Au_{55}Cl_6(PPh_3)_{12}$] was synthesised as described previously.[34] Transmission electron microscopy was performed with a Philips CM 2000 FEG at 200 kV, the electrical measurements were done with a Keithley 6517 ElectroMeter and a Keitheley 2400 SourceMeter in a CryVac cooling system under N_2.

4: A solution of **2** (53 mg, $2.1 \cdot 10^{-4}$ mol) was added dropwise under a nitrogen atmosphere to a stirred solution of [$Au_{55}(PPh_3)_{12}Cl_6$] (100 mg, $7 \cdot 10^{-6}$ mol) in dichloromethane (300 mL). After three weeks, the black precipitate isolated from a colourless solution by filtration was washed carefully several times with CH_2Cl_2 and dried under reduced pressure. Yield 52 mg; Au 58.7, S 11.2.

5, 6, 7: All experiments were performed using the same procedure. Only the solvents were modified, depending on the solubility of the linker: Et_2O for **1**, CH_2Cl_2 for **2**, and DMF for **3**. In a typical experiment, 100 mL of a solution of **1**, **2**, **3** ($2 \cdot 10^{-4}$ mol) was added dropwise to a stirred dichloromethane solution (300 mL) of [$Au_{55}Cl_6(PPh_3)_{12}$] (100 mg, $7 \cdot 10^{-6}$ Mole) under an atmosphere of nitrogen. After addition the reaction was continued for ca. 12 h under an atmosphere of air, leading to a brown precipitate, which was isolated by filtration from the colourless solution. After careful washing with CH_2Cl_2 and the corresponding linker solvent the products (**5**, **6**, **7**) were dried under reduced pressure and used for the electrical measurements.

Product 5: Yield 66 mg; Au 63.6, S 6.17.

Product 6: Yield 78 mg; Au 65.7, S 8.18.

Product 7: Yield 53 mg; Au 65.0, S 6.76.

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