diversity in a quest for superior antifungal agents is apparent on inspection. Efforts to implement this rearrangement as a key simplifying transformation in the total synthesis of the fully elaborated aspirochlorine system will be reported in due course.

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[8] At this stage we leave unspecified the nature of the R---R insert in structures **A**–**C**. The sulfur groups may be separated, directly connected, or connected through a linker.

[9] It is recognized that the species produced from protonation of the ketonic oxygen of quinomethide **B** formally converges with the product of **A** upon acid-induced heterolysis of OL.

[10] For the preparation of **3**, see Ref. [11a], and references therein.

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[12] Refs. [11a] and [11b] include the addition of nucleophiles derived from **3** to primary halides and acid chlorides.

[13] Several preparations of **6** exist; see, for example, Ref. [6b], and references therein.

[14] All new compounds display satisfactory spectroscopic and analytical data consistent with the assigned structures. Crystallographic data (excluding structure factors) for compound **9** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147018. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] Stereochemical assignments of compounds **11** and **12** were based upon similarity of spectroscopic data in comparison to compounds **9** and **10**, respectively. See the Supporting Information.

[16] We use the expression β-face migration as referring to establishment of the S−C(7) bond *syn* to position C(9) of the spiro diketopiperazine substructure.

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[18] A similar stabilizing interaction between a sulfur atom and a carbonyl group was invoked in Ref. [11b].

[19] The arguments advanced above focus on the migrating sulfur atom wherein the sense of rotation around the C(7)−C(8) bond accommodates the preferred modality of sulfur migration. Alternatively, it could be that a preferred sense to the C−C rotation itself serves to determine the face of the sulfur migration.

[20] We note that the observed rearrangement process is suggestive of a possible biosynthesis of aspirochlorine.

Ion-Specific Aggregation in Conjugated Polymers: Highly Sensitive and Selective Fluorescent Ion Chemosensors[**]

Jinsang Kim, D. Tyler McQuade, Sean K. McHugh, and Timothy M. Swager[*]

Conjugated polymers are emerging as versatile elements for the design of chemical sensors.[1, 2] An expansive range of structures is known, and thus the facile tuning of properties by modification of the polymer backbone or the introduction of side groups is possible. A variety of transduction methods that modify the emission and conductivity of a conjugated polymer is available, these include photochemically induced electron transfer, doping, conformational changes, and metal ligation.[1–3] Interchain interactions play a decisive role in controlling the conductive and emissive properties of conjugated polymers in the bulk material.[4] Nevertheless, no sensory system which directly exploits interchain interactions in conjugated polymers has been reported. Herein, we report a new transduction mechanism based on the aggregation of

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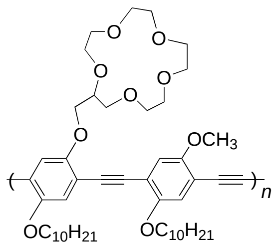
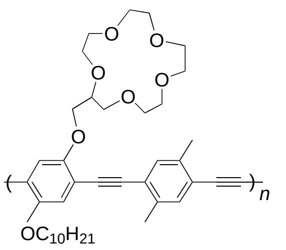
Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

conjugated sensory polymers induced by K$^+$ ions; this new system displays enhanced sensitivity because of energy migration processes and has a high selectivity for K$^+$ over Na$^+$ ions.

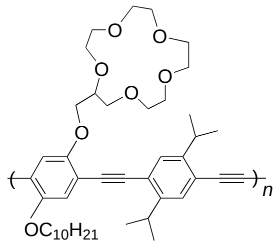
We synthesized the poly(*p*-phenylene ethynylene)s **1**–**4** with the molecular weight (M_n) and polydispersiy index (PDI) shown (2-S and 2-L designate short and long polymers, respectively) by the Sonogashira–Hagihara coupling reaction.[5] We endeavored to design a system in which potassium ions will induce polymer aggregation whereas sodium ions will not so that a selective ion sensor would be produced. To accomplish this we have exploited the well known 2:1 sandwich complex formed between K$^+$ ions and [15]crown-5.[6] Potassium ions cause the polymers to aggregate, thus creating low-energy traps in the electronic structure of the polymer. Energy migration to these traps can result in a large response even at a dilute analyte concentration. Recently several research groups have reported K$^+$ ion sensors based on [15]crown-5 groups in which the response to K$^+$ ions is seen by changes in either the absorbance or the fluorescence spectra of the ionophore.[7] Our new poly(*p*-phenylene ethynylene) systems also have a high sensitivity and offer the advantage of dual detection methods, both UV/Vis and fluorescence spectroscopy can be employed.



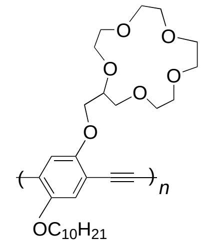
1 M_n = 19 600 PDI = 2.5



2 2-S M_n = 4 700 PDI = 3.1
2-L M_n = 36 000 PDI = 3.2



3 M_n = 66 000 PDI = 1.9



4 M_n = 8 100 PDI = 2.0

Li$^+$ or Na$^+$ ions form 1:1 complexes with [15]crown-5, and exert no observable effect on any of the spectroscopic properties of the polymer. The absorbance and fluorescence spectra of polymer **1** in solution are essentially unchanged even after the addition of a 1500-fold excess of Li$^+$ or Na$^+$ ions. In contrast, addition of K$^+$ ions to a solution of **1** produced a new red-shifted peak at 457 nm in the absorption spectra and also fluorescence quenching was evident (Figure 1). Previous studies in our group and in others provide substantial evidence that the new peak and quenching are the result of interpolymer π-stacking aggregation[4, 8] which, in this case, is induced by K$^+$ ion bridges between two [15]crown-5 units on different polymer chains (Scheme 1).

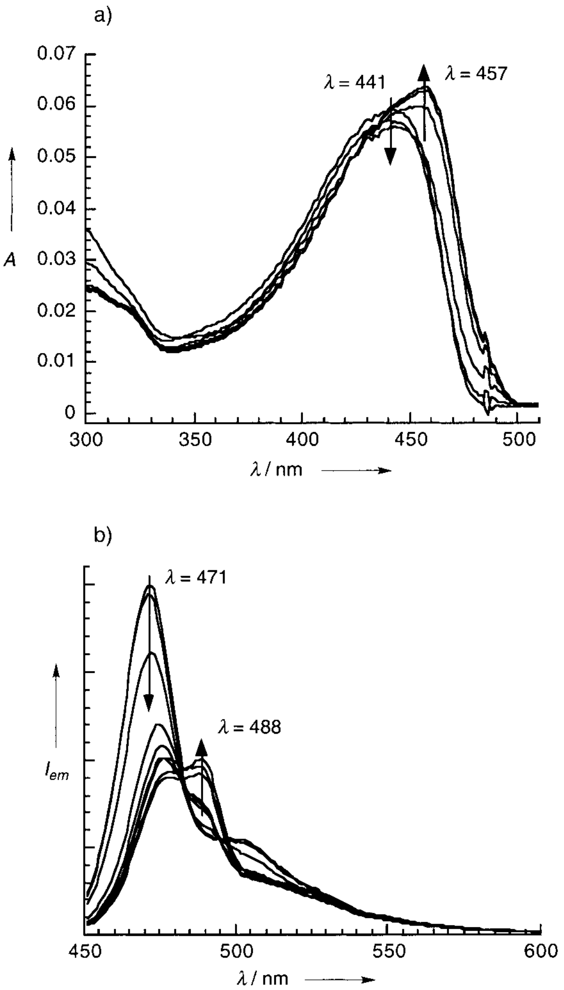
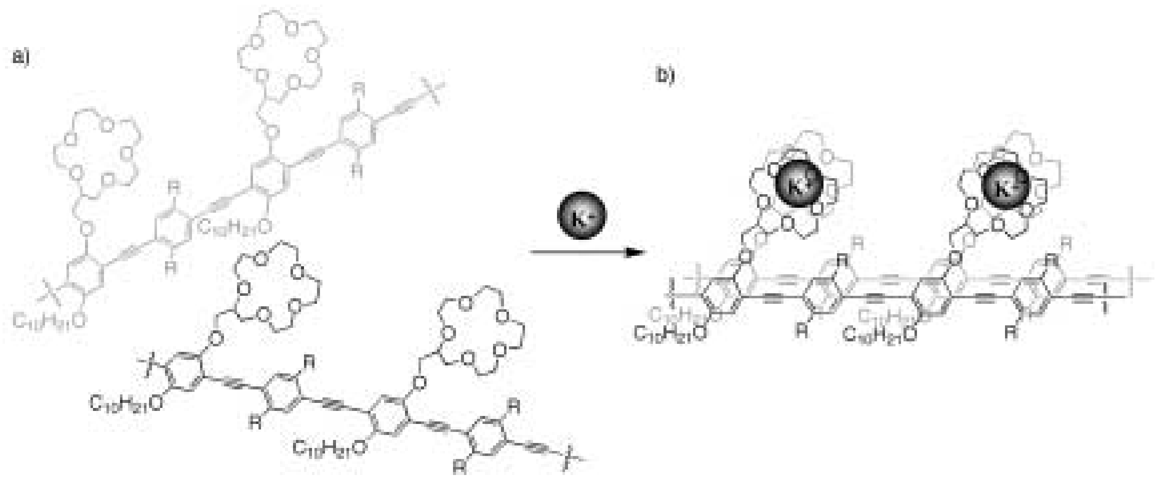


Figure 1. a) Absorbance and b) fluorescence spectra of polymer **1** with various mole ratios of K$^+$ ions. A solution of KPF$_6$ (18 mM) in acetonitrile was added gradually to a solution of the polymer (5 μM, 3.6 mL) in THF. The arrows indicate the changes that result from progressively increasing the concentration ratio of K$^+$ ions to [15]crown-5: [15]crown-5:K$^+$ = 1:0, 1:0.5, 1:1, 1:2.5, 1:5, 1:10, and additionally, for the fluorescence spectra, at 1:20, 1:50, 1:100. The polymer was excited with radiation of λ = 343 nm.

The effectiveness of the interpolymer π-stacking aggregation can be governed by the bulk of the side groups attached to the polymer.[8] Polymer **2** with two methyl groups in every second repeating unit offers the least resistance to the formation of interpolymer π-stacking aggregates, and thus displays the most pronounced aggregation which is noticeable by visual inspection. Of the polymers studied the fluorescent quenching of polymer **2**(2-L) is most sensitive and an 82 % decrease in intensity at 452 nm is observed with a 1:0.5 (5.0 μM:2.5 μM) crown ether:potassium mole ratio (Figure 2). This ion-specific aggregation and consequent fluorescent quenching are stable for extended periods. There was no precipitation and the spectroscopic properties remained unchanged for three weeks at ambient temperature. In the presence of K$^+$ ions polymer **2** is only weakly emissive, with a broad aggregate band centered at 540 nm. The complete disappearance of the peak corresponding to the nonaggregated polymer indicates that much more effective aggregation occurs than in polymer **1** (Figure 2b). One explanation for the



Scheme 1. Schematic representation of the K^+ ion induced aggregation. a) Randomly orientated state; b) π-aggregated state induced by ([15]crown-5)–K^+–([15]crown-5) bridges.

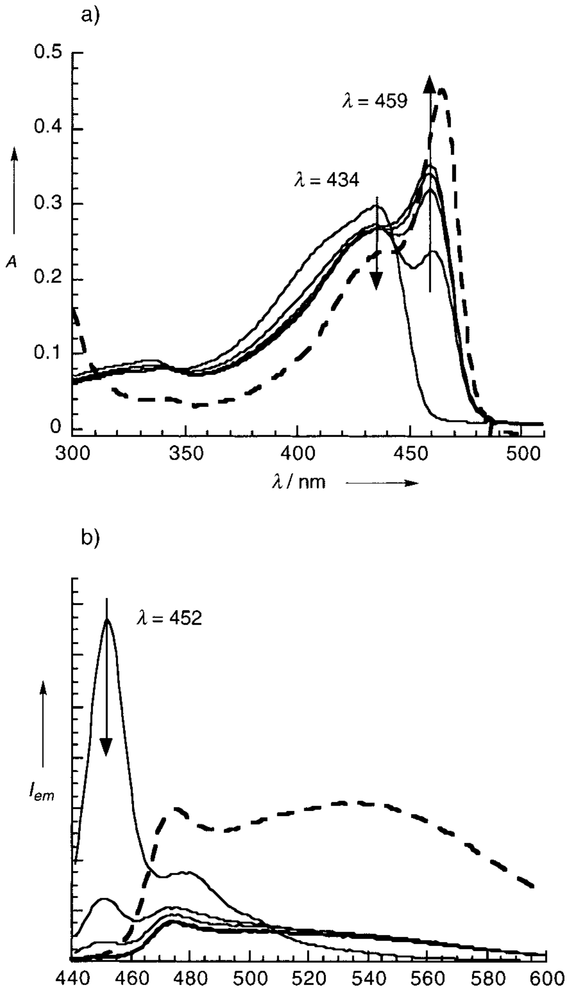


Figure 2. a) Absorbance and b) fluorescence spectra of polymer **2**(2-L) with various mole ratios of K^+ ions. A solution of KPF_6 (18 mM) in acetonitrile was added gradually to a solution of the polymer (5 μM, 3.6 mL) in THF. The arrows indicate the changes that result from progressively increasing the concentration ratio of K^+ to [15]crown-5: [15]crown-5:K^+ = 1:0, 1:0.5, 1:1, 1:2.5, 1:5 and the dashed lines are data from a monolayer Langmuir–Blodgett (LB) film. The intensities of the spectra of the LB films are adjusted for clarity. For the K^+ ion dependent fluorescence spectra the polymer was excited at the pseudo isosbestic point, 343 nm.

lower response of polymer **1** is its ability to form a lariat ether type complexation between [15]crown-5 and the methoxy oxygen atom bound to the phenyl unit of the next repeating unit. This binding competes with the formation of the 2:1 sandwich complex and thereby results in less effective aggregation.

To prove that the sensory response is a result of the interpolymer π-stacking aggregations, we prepared a completely aggregated film of polymer **2**(2-L) by utilizing its surfactant properties and the Langmuir–Blodgett method.[4f, 9] Polymer **2** has hydrophobic decyloxy groups *para* to the hydrophilic [15]crown-5 units, and based upon previously established studies and the extrapolated area per repeating unit (37 Å^2 per phenylene ethynylene unit) we determined that polymer **2**(2-L) forms an edge-on structure at the air–water interface (Figure 3).[4f, 9] Therefore, the conjugated π planes face each other to form π-stacked aggregates The absorption and fluorescence spectra of a monolayer Langmuir–Blodgett film of polymer **2** on a hydrophobic substrate (the dashed lines in Figure 2) are essentially the same as solutions in which aggregation is induced by K^+ ions.

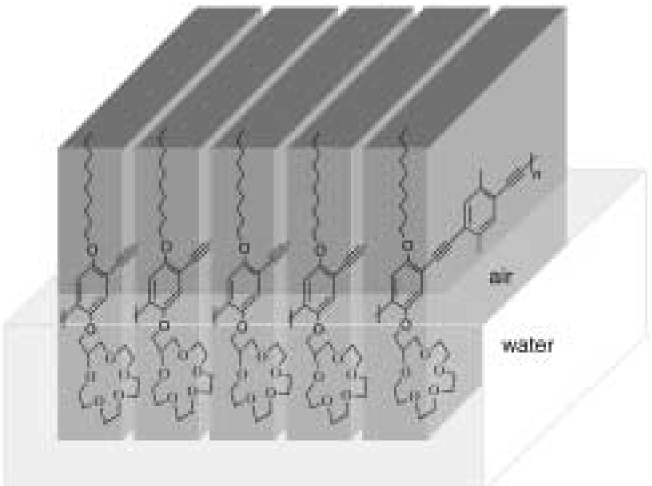


Figure 3. Schematic representaion of the edge-on structure of polymer **2**(2-L) at the air–water interface.

The exciton transport properties of conjugated polymers have been shown to produce amplification of a sensory signal.[1, 10] In this system a longer polymer should have higher sensitivity at low analyte concentration than a shorter polymer. This assertion does require that the excitons are able to sample the entire polymer chain. The lifetime of an exciton and its mobility in polymers, similar to those presented here allows the exciton to sample up to 108 phenylene ethynylene repeating units.[10] In good agreement with these concepts, the higher molecular weight polymer **2** (2-L) revealed a higher sensitivity than the shorter polymer **2** (2-S; Figure 4). However, the amplification effect is less than we expected. The increase in the peaks in the UV/Vis spectra arising from aggregation and the fluorescence quenching both indicate a cooperative response to K^+ ions. We postulate that the initial K^+ ion bridging brings two polymers closer together, thus providing preorganized sites for K^+ ion bridges. Therefore, the formation of further bridges between the two polymers is preferred over aggregation with other isolated polymer chains. Since just a few aggregated sites are needed to quench two polymers, an unnecessary abundance of K^+ ion bridges makes the amplification effect less than in the ideal case in which only the optimum (minimum) number of potassium bridges are formed among polymer chains.

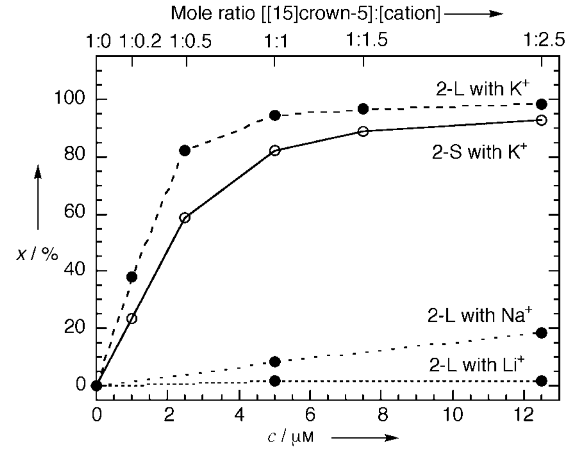


Figure 4. Fluorescence quenching of polymers **2**(2-L) and **2**(2-S) by various concentrations of cations. The ordinate shows the fluorescence quenching $X\%$ $[(I_0 - I)/I_0 \times 100]$; I_0 = fluorescence intensity at 452 nm of a solution of polymer **2** (5 µM) without cations; I = fluorescence intensity at 452 nm of a polymer **2** solution (5 µM) in the presence of cations.

Increasing interchain bulk should stifle interpolymer aggregation and lower the response to potassium ions. To test this hypothesis we synthesized polymer **3** which contains isopropyl groups. Accordingly, the spectra of polymer **3** show no significant changes upon adding Li^+, Na^+, or K^+ ions which indicates that the isopropyl groups are sufficiently bulky to prevent π-stacking aggregation with any ion.[8]

The distance between [15]crown-5 groups in a single polymer chain is also a key design parameter. Surprisingly, polymer **4** with [15]crown-5 groups on every repeating unit is not responsive to K^+, Na^+, or Li^+ ions. An explanation is that the distance between the [15]crown-5 groups in polymer **4** favors, based on entropic considerations, the formation of intrapolymer bridges. The formation of the intrapolymer ([15]crown-5) – K^+ – ([15]crown-5) bridge is favorable according to molecular modeling studies.[11] Polymer **4**, which is not regioregular, can form three isomeric K^+ ion complexes (Figure 5). Polymers **1**, **2**, and **3** with [15]crown-5 groups on every second repeating unit can only form intrapolymer bridges by severe twisting and bending of the polymer backbone. Therefore, intrapolymer binding is unlikely, thus K^+ ions form interpolymer bridges as illustrated in Scheme 1.

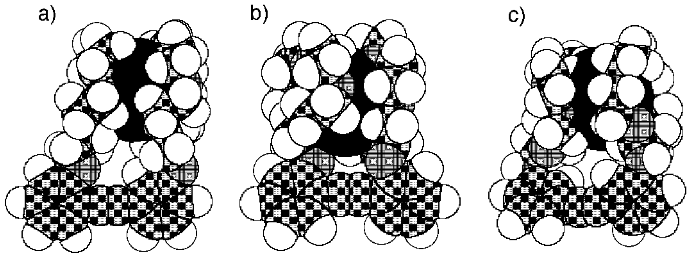


Figure 5. Space-filling models of the potassium complexes of model compounds that represent different regio isomeric dyads in polymer **4**; a) 2,3′-di(oxymethylene [15]crown-5) diphenylethyne; b) 2,2′-di(oxymethylene [15]crown-5) diphenylethyne; c) 3,3′-di(oxymethylene [15]crown-5) diphenylethyne. Hatched circles = oxygen atoms; large black circles = potassium ions.

In summary, we report a highly specific and sensitive transduction mechanism that utilizes ion-mediated interpolymer aggregation. This new system illustrates a general principle that is applicable to multivalent recognition events often found in biological systems.[12]

Detailed experimental conditions and material preparations are available in the Supporting Information.

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[11] All calculations were performed by using the Spartan 5.0 molecular modeling program running on a SGI O2 (R12000) workstation.[11a] Geometry optimizations were performed by using molecular mechanics with MMFF94 force field without constraints.[11b] a) Wavefunction, Inc: 18401 Von Karmann, No. 210, Irvine, CA; b) T. A. Halgren, *J. Comput. Chem.* **1996**, *17*, 490.
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[{Ir(η^5-C_5Me_5)(CO)}$_6$$Hg_8$][$CF_3CO_2$]$_6$, a Mixed-Metal Cluster with an Ir_6Hg_6 Twelve-Membered Ring and Additional Hg Centers and Metal–Metal Bonds**

Giuseppina Chiaradonna, Giovanni Ingrosso,* and Fabio Marchetti*

In 1995 one of us reported that benzene can be directly aminated by diethylamine in the presence of [Ir(η^5-C_5Me_5)(CO)$_2$] (**1**) and a mercury(II) salt, typically $HgSO_4$; one of the roles played by the latter is most probably that of making the carbonyl ligands more susceptible to nucleophilic attack.[1] Accordingly, the literature[2] documents that the interaction of the metal–base[3] **1** with $HgCl_2$ results in a marked shift of the CO stretching frequencies to higher wavenumbers as a consequence of the formation of the adduct [(η^5-C_5Me_5)(CO)$_2$IrHgCl][$HgCl_3$] (**2**). These preliminary remarks prompted us to start an extensive investigation of the reaction of **1** with various mercury(II) salts with the aim of exploring further the chemistry of such a reaction. Hereby, we have discovered a quite complex reactivity which varies markedly on varying the nature of the salt. Herein, we report on the reaction of **1** with $Hg(CF_3CO_2)_2$ in CH_2Cl_2 which yields the unexpected compound [{Ir(η^5-C_5Me_5)(CO)}$_6$$Hg_8$][$CF_3CO_2$]$_6$ (**3**) as a red crystalline diamagnetic solid. The course of the reaction is still unclear; however, the definite nature of **3** clearly indicates an oxidative role played by the Hg^{2+} ion. Although transition metal compounds containing bonds with mercury have been known for a long time, mercury clusters are relatively rare[4] and the structure of **3** is unique in this field.

The ^{1}H NMR spectrum of compound **3** exhibits two sharp singlets at $\delta = 2.28$ and 2.53 ([D]chloroform) in a 2:1 ratio for two sets of magnetically equivalent η^5-C_5Me_5 methyl groups, both being downfield from the value for **1** ($\delta = 2.18$, [D]chloroform).[5] The IR spectrum of **3** shows four CO stretching frequencies at 1972, 1957, 1948, and 1935 cm^{-1} (nujol) that are lower than those for **1** (2000 and 1925 cm^{-1}).[5] Thus, a comparison of the ^{1}H NMR and IR data for **3** with those reported for **2** (i.e. $\delta = 2.31$, and ν(CO) = 2085 and 2045 cm^{-1}[2]) provides evidence in favor of increased electron density at the iridium centers in **3**. Thus, the nature of the Ir–Hg bonds in **3** is significantly different from that in **2**. In fact in **2**, the metal–metal bond causes a withdrawal of electron density from the iridium center.[2]

The molecular geometry of **3** was determined by single-crystal X-ray analysis at 293 K (Figure 1). The cationic component of **3**, that is [{Ir(η^5-C_5Me_5)(CO)}$_6$$Hg_8$]$^{6+}$, contains a novel ring system with an Ir_6Hg_6 twelve-membered ring with additional Hg centers; Hg–Hg and Hg–Ir bonds give rise to a network within the Ir_6Hg_6 ring. The whole metal network appears roughly disposed on three different planes bent in a way which is reminiscent of the chair conformation of cyclohexane. The core moiety of [{Ir(η^5-C_5Me_5)(CO)}$_6$$Hg_8$]$^{6+}$ (Figure 2), formed by the Hg(1), Hg(2), Ir(1), Ir(3), Hg(1'), Hg(2'), Ir(1'), and Ir(3') metal centers, is almost exactly planar with a maximum deviation of 0.04 Å. Interestingly, the same fascinating arrangement[6] has al-

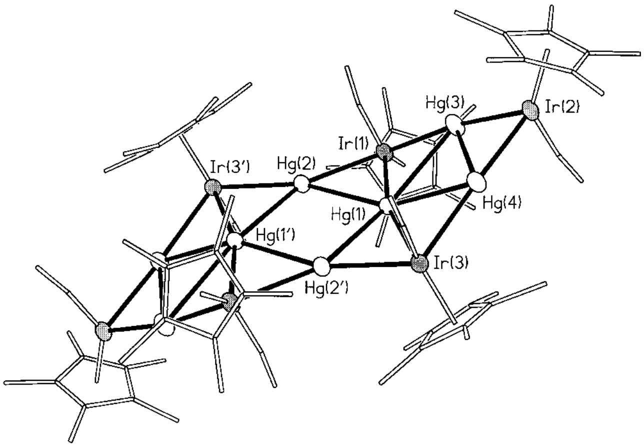

Figure 1. The molecular structure of the cation in **3**. The $CF_3CO_2^-$ ions and H atoms are omitted for clarity. The metals are represented by thermal ellipsoids at 30% probability. The superscript ' denotes the atoms generated by the symmetry operation $1-x, 1-y, -z$. Metal–metal bond lengths [Å] (standard deviations are given in parentheses): Hg(1)-Ir(1) 2.739(2), Hg(1)-Ir(3) 2.749(2), Hg(1)-Hg(2') 2.982(2), Hg(1)-Hg(2) 3.0278(18), Hg(1)-Hg(3) 3.070(2), Hg(1)-Hg(4) 3.078(2), Hg(2)-Ir(1) 2.675(2), Hg(2)-Ir(3') 2.679(2), Hg(2)-Hg(1') 2.982(2), Hg(3)-Ir(2) 2.599(2), Hg(3)-Ir(1) 2.685(2), Hg(3)-Hg(4) 2.962(2), Hg(4)-Ir(2) 2.604(2), Hg(4)-Ir(3) 2.701(2).

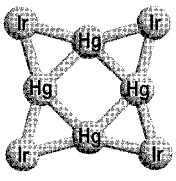

Figure 2. The Hg_4Ir_4 core moiety of [{Ir(h^5-C_5Me_5)(CO)}$_6$$Hg_8$]$^{6+}$.

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