systems, USA). The emmission spectra of the two dyes were recorded at intervals of 0.5–0.7 s (FAM: $\lambda_{max} = 535$ nm, TAMRA: $\lambda_{max} = 582$ nm, excitation wavelength: 488 nm). All experiments were done in triplicate. By plotting the relative fluorescence of the fluorophore (ΔR_n value) at 535 nm against time, the proportion of cleaved RNA substrate versus negative control (identical experiment with inactive HHR1mut-DNA instead of HHR1-DNA) was determined. The raw data were imported into Microsoft Excel, computed, and further processed.

To eliminate unspecific fluorescence effects it had to be taken into account that the absolute, but not the percental, deviation in fluorescence increases with the increase in fluorescence during the catalytic cleavage. The time course of the cleavage was corrected by the percental deviation of the curve obtained for the negative control experiments from the value at $t = 0$ according to Equation (1) ($F_{korr}(t)$: corrected fluorescence at a given time point t; $F_{neg}(t)$: fluorescence of the negative control at a given time point t; $F_{neg}(t_0)$: fluorescence of the negative control at $t = 0$; $F_{HHR}(t)$: increase in fluorescence in the presence of transcribed HHR at a given time point t).

$$F_{korr}(t) = \frac{F_{neg}(t)}{F_{neg}(t_0)} F_{HHR}(t) \qquad (1)$$

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Exploiting Incommensurate Symmetry Numbers: Rational Design and Assembly of $M_2M'_3L_6$ Supramolecular Clusters with C_{3h} Symmetry[**]

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There are many elegant oligomeric or polymeric structures based on metal–ligand interactions that lead to well-organized supramolecular architectures. Examples include extended arrays[1–7] in two or three dimensions and discrete clusters of various types.[8–30] However, relatively few such clusters have been the result of predictive design. We have developed a rational design for the synthesis of high-symmetry clusters using coordination number incommensurate interactions. Resultant examples include M_2L_3 helicates[15, 24, 31, 32] and their *meso*-counterparts (mesocates),[32] and M_4L_6[12, 33–35] and M_4L_4[36] tetrahedra. In these clusters, three bidentate chelators coordinate a tri- or tetravalent metal ion in a pseudo-octahedral fashion to generate a threefold axis, and a symmetric, multi(bidentate) ligand generates the other symmetry element (twofold,[15, 24, 31, 32] threefold,[36] or mirror plane[32]).

Here we present the rational design of a mixed-metal cluster in which, rather than deriving one symmetry element

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from a symmetric ligand, two different metals are used to generate the two incommensurate symmetry elements (Figure 1). This forms the basis for coordination number incommensurate cluster formation.[37] In principle, the ligand forms part of an asymmetric unit of the cluster and must have two different interaction sites (e.g., one hard and one soft donor) that can each preferentially interact with one of the metal ions over the other.

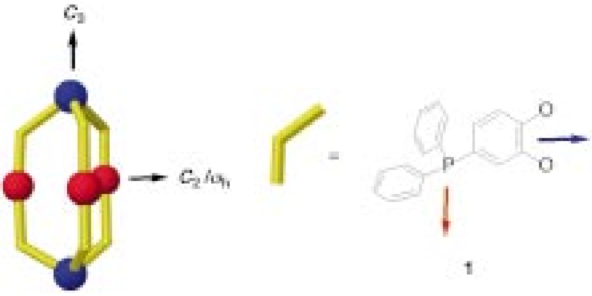


Figure 1. Cartoon showing the 90° offset, incommensurate interaction of a threefold symmetry element and a C_2 axis/mirror plane to generate a $M_2M'_3L_6$ cluster. Blue spheres represent trivalent or tetravalent metals coordinated to the catechol funtionality of **1**, red spheres are $PdBr_2$ fragments coordinated to the phosphane of **1**.

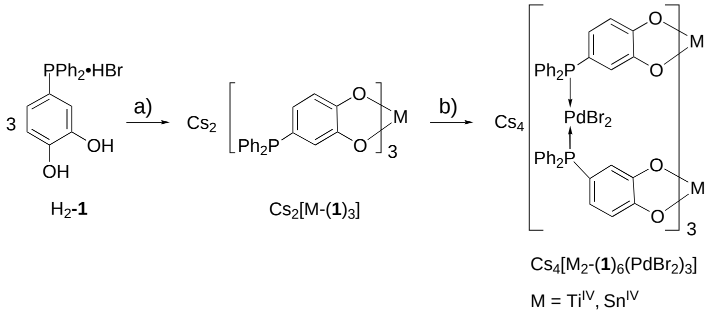
A chiral triple-helicate has idealized D_3 symmetry, while an achiral triple-mesocate has C_{3h} symmetry. To synthesize a mixed-metal helicate (or mesocate) of stoichiometry $M_2M'_3L_6$, a threefold interaction site and an orthogonal twofold (mirror plane) interaction site must be generated (Figure 1).[38]

Catechol ligands are relatively hard donors and generate a C_3 axis when forming a tris-chelate with hard, tri- or tetravalent metals (e.g., Al^{III}, Ga^{III}, Fe^{III}, Sn^{IV}, Ti^{IV}).[39, 40] Phosphane ligands, on the other hand, are soft donors and can generate a twofold axis or mirror plane when coordinated in a *trans* fashion to metals with square-planar geometry (e.g., Pd^{II} or Pt^{II}).[41, 42] A hybrid ligand containing both these functionalities arranged in the proper geometry can, if properly designed, generate an $M_2M'_3L_6$ cluster, because it is the smallest discrete species that would simultaneously fulfill the two 90° offset, incommensurate symmetry requirements.

While the phosphanyl and quinonic functional groups would be mutually incompatible,[43–45] several reports of 2-phosphanyl-substituted *p*-dihydroquinones have appeared in the literature.[46–48] These were designed to optimize metal chelation by the phosphane/phenolate donor set. For our purposes, a 4-phosphanylcatechol ligand was suggested by molecular modeling[49] as having the ideal geometry for isolating the two types of coordination sites and permitting cluster assembly. To determine the type of cluster (mesocate or helicate) that would form, molecular modeling[49] studies were performed on $Cs_4[Ti_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$. The results indicated that the mesocate has a larger Ti ⋯ Ti separation (6.5 Å compared to 6.1 Å for the helicate) and a substantially lower energy by 26 kcal mol^{-1}.

The readily-prepared hybrid ligand 4-PPh_2-catechol (H_2-**1**)[50] was employed to synthesize the tris-(4-PPh_2-catecholate) complexes $[M\text{-}(\mathbf{1})_3]^{2-}$ (M = Ti, Sn).[51] In each case, a single set of resonances was observed in the ^{31}P, ^{1}H, and ^{13}C NMR spectra even when the sample was cooled to −60 °C. This is consistent with the selective formation in solution[52] of only the *fac* isomer with C_3 symmetry rather than the C_1-symmetric, *mer* isomer, which should be statistically favored by a 3:1 ratio.

Reaction of two equivalents of $Cs_2[Ti\text{-}(\mathbf{1})_3]$ and three of $PdBr_2 \cdot 2\,PhCN$ in DMF gives an orange solution from which an orange-red solid can be isolated in good yield (95 %, Scheme 1). Solution ^{31}P, ^{1}H and ^{13}C NMR spectra reveal the formation of a single product with high symmetry.



Scheme 1. Synthesis of the C_{3h}-symmetric, mixed-metal mesocates. a) Cs_2CO_3, $[Ti(OMe)_4]$ or $SnCl_4$/methanol; b) 1.5 equiv $PdBr_2 \cdot 2\,PhCN$/DMF.

Further, the observation of virtual $^{13}C\{^{1}H\}$ triplet resonances for both catecholate and phenyl ring carbon atoms is consistent with a *trans*-phosphane coordination of a Pd^{II} center. This *trans* coordination also results in strong $^{2}J(P,Pd,P)$ couplings.[53] The FAB^{+} mass spectrum indicates formation of a $[Ti_2\text{-}(\mathbf{1})_6Pd_3]^{2+}$ ion associated with varying numbers of cesium cations and bromine anions.

A single-crystal X-ray diffraction study confirms the structure of this heterometallic assembly.[54] The cluster has crystallographically imposed C_{3h} symmetry (Figure 2). The cluster, therefore, is an achiral mesocate with one titanium atom having Δ and the other having Λ configuration. The Ti ⋯ Ti separation is 6.76 Å. The three Pd centers have distorted square-planar geometries and *trans*-coordinated phosphane ligands. Of particular interest is the location of the Cs^{+} ions: three of them are embedded in the three clefts of the cluster and are coordinated by four *endo*-catecholate oxygen atoms in a rectangular array and two *exo*-molecules of THF solvent (Figure 3). The depth of these clefts is such that the THF

Figure 2. A stereographic representation (side view) of $[Ti_2\text{-}(\mathbf{1})_6\text{-}(PdBr_2)_3]^{4-}$. The Cs counterions, hydrogen atoms, and solvent molecules are omitted for clarity. The pink spheres represent Pd atoms, brown spheres are Br atoms, and orange spheres are Ti atoms. The wireframe represents the ligand with carbon atoms shown in gray, phosphorus atoms in yellow, and oxygen atoms in red.

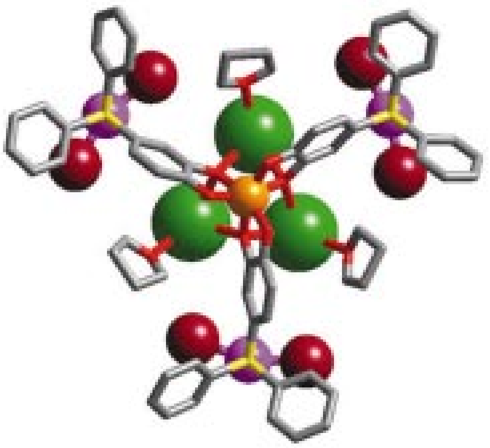


Figure 3. A view of $Cs_4[Ti_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$ down the crystallographic threefold axis of the cluster. One disordered Cs atom and all disordered solvent molecules and hydrogen atoms were omitted for clarity. The color scheme is the same as that in Figure 2, with Cs atoms represented by green spheres.

molecules can also be described as being buried. The low coordination number (6) of the cesium cations can be explained by the position of the peripheral bromine atoms: while not in van der Waals contact with the cesium cations, the Cs atoms are shielded from additional coordination by the Br atoms (Figure 3).

The heterometallic cluster can also be prepared as the Sn^{IV} analogue. Reaction of two equivalents of $Cs_2[Sn\text{-}(\mathbf{1})_3]$ and three of $PdBr_2 \cdot 2PhCN$ in DMF gives a single red product, $Cs_4[Sn_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$. The crystal structure of this compound has also been determined (Figure 4).[55] Although not crystallographically imposed, the molecule has idealized C_{3h} symmetry similar to the Ti^{IV} complex described above. Three of the cesium cations are also located in the cluster clefts, but one of the bromine atoms from each of the three palladium centers is deflected in towards the cluster cavity and coordinates a cesium atom (Figure 5). The second bromine atom on each of the three palladium centers is deflected out from the cluster interior. The Sn$\cdots$Sn separation is 6.88 Å, 0.12 Å larger than that for the Ti structure (vide supra). This increased separation, due to the larger ionic radius of Sn^{IV} compared to Ti^{IV} (0.830 Å and 0.745 Å, respectively),[56] may allow the observed Cs$\cdots$Br interactions to occur within the clefts of this cluster but not in the Ti analogue.

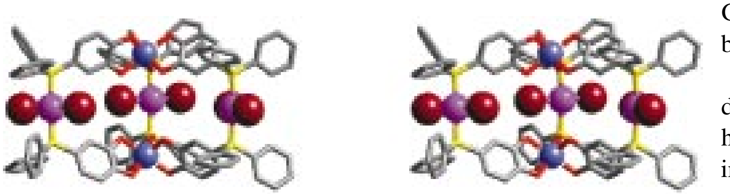


Figure 4. Stereographic representation (side view) of $[Sn_2\text{-}(\mathbf{1})_6(PdBr_2)_3]^{4-}$. The Cs counterions, hydrogen atoms, and solvent molecules are omitted for clarity. The pink spheres represent Pd atoms, brown spheres are Br atoms, and blue spheres are Sn atoms. The wireframe represents the ligand with carbon atoms shown in gray, phosphorus atoms in yellow, and oxygen atoms in red.

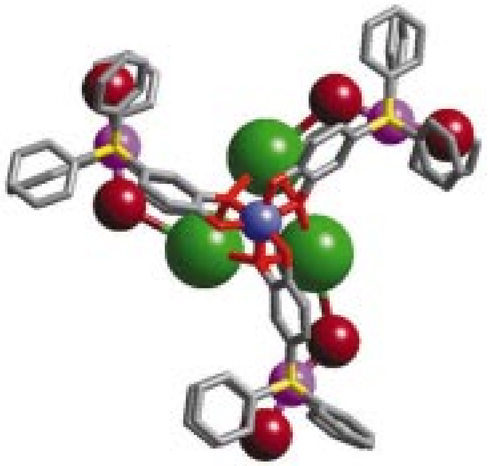


Figure 5. A view of $Cs_4[Sn_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$ down the pseudo threefold axis of the cluster. All disordered solvent molecules, all hydrogen atoms, and one of the disordered Cs atoms are omitted for clarity. The color scheme is the same as that in Figure 4, with Cs atoms represented by green spheres.

Computer modeling studies of both clusters have demonstrated that the $M^{IV}\cdots M^{IV}$ distances are shorter in the helicate than in the mesocate (vide supra). In addition, only three *endo*-catecholate oxygen atoms are available for Cs^+ coordination at each of the three molecular clefts of the helicate compared to four for the mesocate. Thus, the mesocate provides a better coordination environment for the large Cs counterion. Therefore, the use of a smaller alkali metal cation may induce helix formation. There is already some indication that there is indeed a cation effect in cluster formation: the use of triethylammonium as the cation in the synthesis of the Ti cluster leads to the presence of two different species which can be converted back to the C_{3h} mesocate upon addition of CsOTf ($Tf = F_3CSO_2$). These cation effects are currently being investigated.

Our successful realization of this example of symmetry driven cluster formation augurs well for the future use of hybrid ligands and disparate metal coordination preferences in the generation of a variety of novel, mixed-metallic, supramolecular assemblies.

Experimental Section

All NMR spectra were measured with a Bruker 360 MHz or a JEOL FX-90Q spectrometer. Chemical shifts of ^1H and ^{13}C spectra are reported as δ downfield from TMS. The ligand $H_2\text{-}\mathbf{1} \cdot HBr$ has been fully characterized by NMR spectroscopy and elemental analysis. Reactions were performed under an atmosphere of purified nitrogen using standard Schlenk techniques.

$Cs_4[Ti_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$: A solution of $Cs_2[Ti\text{-}(\mathbf{1})_3]$ (0.42 g, 0.35 mmol) and $PdBr_2 \cdot 2PhCN$ (0.25 g, 0.53 mmol) in DMF (20 mL) was stirred at room temperature for 2 h. Initial turbidity readily disappeared to give a clear, orange solution. Addition of THF precipitated an orange-yellow solid which was isolated in 95 % yield. The solid was redissolved in DMF/THF (1:10) and slow diffusion of diethyl ether into this solution gave well-formed, orange-red crystals suitable for single-crystal X-ray diffraction studies. Elemental analysis: calcd for $C_{108}H_{78}Br_6Cs_4O_{12}P_6Pd_3Ti_2 \cdot 2.5\,DMF \cdot 3.5\,H_2O$ (%): C 40.55, H 3.05, N 1.12; found: C 40.92, H 3.00, N 0.76; ^1H NMR (360 MHz, $[D_7]$DMF, TMS): $\delta = 7.89$ (t, $J = 6.4$ Hz, 1H, catechol), 7.63 (m, br d, 4H, phenyl), 7.37 (m, br d, 6H, phenyl), 6.40 (br d, 1H, catechol), 6.25 (d, $J = 7.9$ Hz, 1H, catechol); $^{13}C\{^1H\}$ NMR (89.9 MHz, $[D_7]$DMF, TMS): $\delta = 163.8$ (s, catechol), 159.8 (t, $J(P,C) = 10.3$ Hz, catechol), 134.7 (t, $J(P,C) = 5.6$ Hz, phenyl), 134.4 (t, $J(P,C) = 20.2$ Hz, phenyl), 129.7 (s, phenyl), 127.6 (t, $J(P,C) = 5.0$ Hz, phenyl), 124.9 (s, catechol), 121.9 (t, $J(P,C) = 13.9$ Hz, catechol), 115.7 (t, $J(P,C) = 28.2$ Hz, catechol), 111.0 (t, $J(P,C) = 6.0$ Hz, catechol); $^{31}P\{^1H\}$ NMR (36.3 MHz, $[D_7]$DMF, 85% H_3PO_4): $\delta = 22.11$(s); positive ion FAB-MS: m/z (nitrobenzyl alcohol, $\blacklozenge = [Ti_2\text{-}(\mathbf{1})_6Pd_3]^{2+}$): m/z (m/z_{calcd}): 3311 (3312.6) $[\blacklozenge + 6\,Br^- + 5\,Cs^+]$, 3179 (3180.7) $[\blacklozenge + 6\,Br^- + 4\,Cs^+ + 1\,H^+]$, 3101 (3099.8) $[\blacklozenge + 5\,Br^- + 4\,Cs^+]$, 3049 (3048.8) $[\blacklozenge + 6\,Br^- + 3\,Cs^+ + 2\,H^+]$, 2968 (2967.9) $[\blacklozenge + 5\,Br^- + 3\,Cs^+ + 1\,H^+]$, 2886 (2887.0) $[\blacklozenge + 4\,Br^- + 3\,Cs^+]$, 2835 (2836.0) $[\blacklozenge + 5\,Br^- + 2\,Cs^+ + 2\,H^+]$, 2807 (2807.0) $[\blacklozenge + 6\,Br^- + 1\,Cs^+ + 3\,H^+ + 1\,Na^+]$, 2755 (2755.1) $[\blacklozenge + 4\,Br^- + 2\,Cs^+ + 1\,H^+]$, 2675 (2675.1) $[\blacklozenge + 6\,Br^- + 4\,H^+ + 1\,Na^+]$.

$Cs_4[Sn_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$: Similarly prepared from $Cs_2[Sn\text{-}(\mathbf{1})_3]$ in 90% yield. Slow diffusion of diethyl ether into a DMF/THF (1:1) solution of this complex gave well-formed, X-ray diffraction quality, orange-red single crystals. Elemental analyses: for $C_{126}H_{120}Br_6N_6Cs_4O_{18}P_6Pd_3Sn_2$ (%): C 40.25, H 3.22, N 2.24; found: C 40.11, H 3.11, N 2.21; ^1H NMR (360 MHz, $[D_7]$DMF, TMS): $\delta = 8.16$ (td, $J = 7.3$, 1.7 Hz, 1H, catechol), 7.66 (m, 4H, phenyl), 7.38 (m, 6H, phenyl), 6.58 (d, $J = 7.9$ Hz, 1H, catechol), 6.41 (br d, 1H, catechol); $^{13}C\{^1H\}$ NMR (89.9 MHz, $[D_7]$DMF, TMS): $\delta = 156.2$ (s, catechol), 151.5 (t, $J(P,C) = 10.0$ Hz, catechol), 134.9 (t, $J(P,C) = 5.6$ Hz, phenyl), 134.2 (t, $J(P,C) = 24.9$ Hz, phenyl), 129.8 (s, phenyl), 127.6 (t, $J(P,C) = 5.0$ Hz,phenyl), 123.8 (br d, catechol), 114.7 (t, $J(P,C) = 28.2$ Hz, catechol), 113.4 (t, $J(P,C) = 4.0$ Hz, catechol); $^{31}P\{^1H\}$ NMR (36.3 MHz, $[D_7]$DMF, 85% H_3PO_4): $\delta = 21.27$ (s).

X-ray crystallography:[54, 55] Crystal data for both compounds were collected using a Siemens SMART[57] diffractometer equipped with a CCD area detector using $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. Data in the frames corresponding to an arbitrary hemisphere of data were integrated using SAINT.[58] Data were corrected for Lorentz and polarization effects. An empirical absorption correction based on the measurement of redundant and equivalent reflections and an ellipsoidal model for the absorption surface was applied using XPREP[59] (Sn^{IV} structure) or SADABS[60] (Ti^{IV} structure). The structure solution and refinement for the Sn^{IV} structure was performed using the teXsan[61] crystallographic software package (refining on F); for the Ti^{IV} structure the initial solution was performed using teXsan, but the final refinements were performed using SHELXTL[59] (refining on F^2). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-103117 ($Cs_4[Sn_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$) and CCDC-103118 ($Cs_4[Ti_2\text{-}(\mathbf{1})_6(PdBr_2)_3]$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[52] A crystal structure of $Cs_2[Ti\text{-}(\mathbf{1})_3]$ shows it to be the *mer* isomer: X. Sun, D. W. Johnson, D. L. Caulder, R. E. Powers, K. N. Raymond, E. H. Wong, unpublished results.

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[54] $Cs_4[Ti_2\text{-}(\mathbf{1})_6(PdBr_2)_3]\cdot 9\,THF\cdot H_2O\cdot 3/2\,Et_2O\cdot 3/2\,DMF$: crystal size $0.38\times 0.30\times 0.30$ mm; $T=-122\,^\circ C$; hexagonal space group $P6_3/m$ (no. 176), $a=20.4769(1)$, $b=20.4769(1)$, $c=21.9982(1)$ Å, $V=7988.15(7)$ Å^3, $Z=2$, $\rho_{calcd}=1.711\ g\,cm^{-3}$, $\mu=2.953\ mm^{-1}$, $F(000)=4082$, $2\Theta_{max}=52.28°$. Of the 38263 reflections which were collected, 5129 were unique ($R_{int}=0.044$); equivalent reflections were merged. Empirical absorption correction: $T_{max}=0.429$, $T_{min}=0.341$. One of the Cs counterions, one of the bromine atoms, and much of the solvent were disordered; details can be found in the supporting information. The non-hydrogen atoms (excluding disordered solvent molecules and minor components of the disordered bromine) were refined anisotropically. Hydrogen atoms were included on all but the solvent molecules but not refined. Final $R1=\Sigma(|F_o|-|F_c|/\Sigma|F_o|=0.0579$ for 3950 for $I>2\sigma(I)$ (307 paramaters, 1 restraint); for all 5129 data, $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}=0.1300$. Weighting scheme: $w=1/[\sigma^2(F_o^2)+(0.0356\,P)^2+62.28\,P]$, where $P=(\max(F_o^2,0)+2\,F_c^2)/3$.

[55] $Cs_4[Sn_2\text{-}(\mathbf{1})_6(PdBr_2)_3]\cdot 5\,DMF\cdot 2\,H_2O\cdot THF\cdot x\,solvent$: crystal size $0.10\times 0.11\times 0.15$ mm; $T=-110\,^\circ C$; triclinic space group $P\bar{1}$ (no. 2), $a=18.0134(3)$, $b=18.5299(3)$, $c=28.6388(1)$ Å, $\alpha=99.494(1)$, $\beta=98.315(1)$, $\gamma=119.077(1)$, $V=7954.9(2)$ Å^3, $Z=2$, $\rho_{calcd}=1.59\ g\,cm^{-3}$, $\mu=3.157\ mm^{-1}$, $F(000)=3160$, $2\Theta_{max}=46.5°$. Of the 36575 reflections which were collected, 22133 were unique ($R_{int}=0.068$); equivalent reflections were merged. Empirical absorption correction: $T_{max}=0.776$, $T_{min}=0.521$. One of the Cs counterions and much of the solvent were disordered; details can be found in the supporting information. The non-hydrogen atoms (excluding the disordered Cs atom and disordered solvent molecules) were refined anisotropically. Hydrogen atoms were included on all but the solvent molecules but not refined. Additionally, all phenyl rings were refined as rigid groups. Final $R=\Sigma(|F_o|-|F_c|/\Sigma|F_o|=0.090$ for 12552 data for $I>3\sigma(I)$ (822 parameters, 18 restraints), $Rw=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{1/2}=0.107$. Weighting scheme: $w=1/\sigma^2(F_o)=4\,F_o^2/\sigma^2(F_o^2)$.

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