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A Simple Model for Chromonic Aggregation

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A simple 2-dimensional model is introduced to study molecular stacking in planar-non-ionic chromonics. The model allows changes in aggregation, arising from changes in interaction regions within a chromonic molecule, to be quantified. Application of the model to a typical hydrophobic core – hydrophilic corona molecule, such as the triphenylene-based chromonic TP6EO2M, shows the energetically preferred stacking arrangement of molecules is dependent on the preferred inter-molecule separation and the relative sizes of the triphenylene core and poly(ethylene-glycol) corona. Further, we show a minimum aromatic core size is required to form chromonic phases, explaining why functionalised benzene rings do not form chromonic phases.

Keywords non-ionic chromonic; theory.

Introduction

Chromonic mesogens are non-conventional amphiphiles [1], which self-assemble in aqueous solution to form aggregate structures: rods [2], stacks [3] or layers [4]. These aggregates can subsequently self-organise to form chromonic mesophases. Initial self-assembly is strikingly different to that seen in most conventional amphiphiles: typically being promoted by the interaction of aromatic ring systems and taking place in the absence of a critical micelle concentration. The driving force for chromonic aggregation is hotly debated. For different chromonic systems, static charges, polar and quadrupolar interactions [5], microphase segregation and entropic contributions to the hydrophobic effect have all been claimed to be significant [6].

Chromonic molecules come in a plethora of shapes and sizes, with a few uniform characteristics: namely, a rigid core, often regarded as disc-shaped, and pendant solubilising groups. Most known chromonics are ionic in the sense that the aggregating species is a large molecular ion. The majority of well-studied systems have tended to be anionic [7], but a few cationic examples exist also [8]. The rigid core is usually composed of multiple aromatic rings, with charged solubilising groups, such as carboxylate or sulfonate. The counter ion affiliated with the solubilising group is associated in the crystal form, but, in solution fully solvates and interacts minimally with the chromonic aggregate [9].

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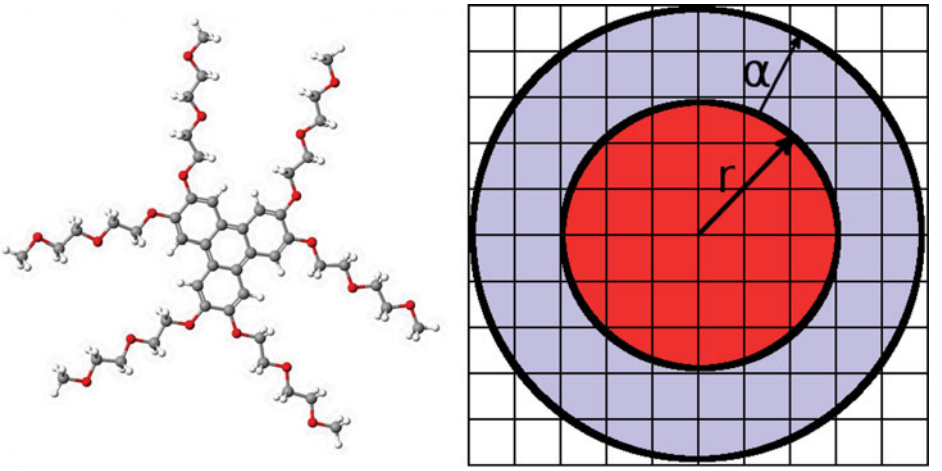

Figure 1. A TP6EO2M molecule (left) and a discretized 2-dimensional representation of a chromonic molecule on a 10×10 grid (right).

Non-ionic chromonics are a separate family of chromonic molecules with similar characteristics to their ionic counterparts. Here, solubilising groups are composed of non-ionic hydrophilic groups such as polyethylene oxide. The molecule 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)-triphenylene, TP6EO2M [10,11,12] (Fig. 1) is an example of a typical non-ionic chromonic: a triphenylene core provides a rigid hydrophobic disc, while a corona of six ethylene oxide arms provide a level of solubility in water.

In principle, one might expect a simple substituted phenyl ring (a benzene core substituted with multiple solubilising groups) to behave as the smallest possible non-ionic chromonic. The smaller size of a substituted benzene molecule, in comparison with a substituted triphenylene molecule, would have favourable properties such as reducing the cross sectional area of a column and hence increasing the aspect ratio of an aggregate. An aggregate with a large aspect ratio should form a nematic phase at a lower density and hence at a lower concentration. However, to date, no chromonic behaviour has been reported for a substituted phenyl ring. The natural explanation for this is the association energy for two phenyl rings is too small for a chromonic phase to exist within the accessible temperature range of the solvent (water).

The interaction between two phenyl rings is often used as a simple model to study the nature of the π-π interaction (an interaction critical in, for example, stabilising the double helix of DNA [13]) but is known to be non-trivial to study accurately, either experimentally or computationally. The π-electrons, present in benzene, require high level simulations, such as *ab initio* calculations at the CCSD(T) level, to accurately reflect their highly correlated nature [14, 15]. In general benzene itself has two strongly bound configurations: T-shaped [16], where the vectors defining the plane of each benzene ring are orthogonal, and parallel-displaced [17], where the two rings are parallel and the vector between the two centre of masses is not identical to the vector defining the plane of the rings (see Fig. 2). In chromonic systems only the parallel-displaced configuration leads to the formation of chromonic phases. To use high level *ab initio* simulations to study the formation of chromonic molecule dimers remains extremely computationally demanding, even with the best computational resources available today. Hence, a simplified approach is required.

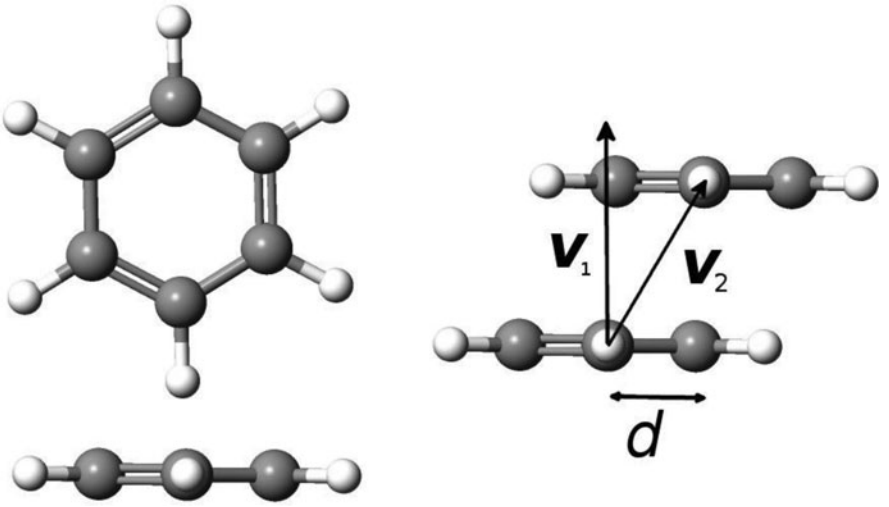

Figure 2. The configuration of a T-shaped benzene dimer (left), and a parallel-displaced benzene dimer (right), where $\boldsymbol{\nu_1}$ is the unit vector normal to the parallel rings, $\boldsymbol{\nu_2}$ is the unit vector between the two centres of masses, and d is the displacement distance.

In this report we introduce a simple 2-dimensional model to study molecular stacking in planar-non-ionic chromonics, and use the model to study stacking in molecules of the TP6EO2M type. We assume that while van der Waal's interactions will be present between two chromonic molecules, they will be of similar magnitude per unit area across the disc. In this case the dominant interaction in terms of determining the arrangement of a disc in a chromonic stack is electrostatic in nature. In the model, each disc has a core unit with a set charge density and a corona with a cancelling charge density, resulting in a non-ionic species. This model captures well the type of electrostatic interactions seen in 2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl)-triphenylene, TP6EO2M molecule (Fig. 1), or in a substituted benzene molecule, by simply adjusting the size (and charge) of the core and corona units.

While this paper concentrates on TP6EO2M, the basic model can easily be extended to include many chromonic molecules of the core/corona type, including those molecules where neither core or corona are circular. Moreover, although we concentrate on the effects of Coulombic interactions, mimicking quadrupolar, dipolar and static charges on the interaction potential. In principle the model can be extended to include cases where the van der Waal's interactions per unit area are not the same, i.e. where van der Waal's interactions specifically favour microphase segregation.

Computational Model

A two dimensional disc with radius, r, and corona size, α, is discretized to fit within a 100 by 100 grid (see Fig. 1 which shows a 10 by 10 grid for clarity). A unit charge is placed at the centre of each grid element. The grid is composed of one of three charges, 0 for grid units outside the corona radius, $+a$ for grid units located in the corona and $-b$ for grid units located in the core. The size of the charges a and b were set such that the complete

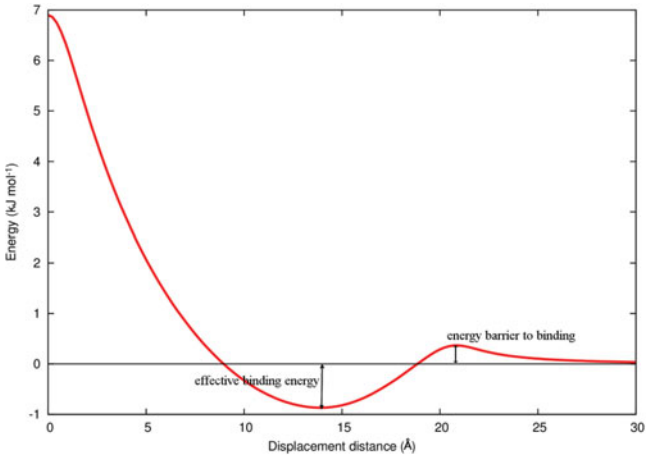

Figure 3. Example binding potential showing the effective binding energy and the energy barrier to binding.

system has a zero total charge ($an_a = bn_b$ where n_a is the number of grid components with charge a and n_b is the number of grid components with charge $-b$). The disc was replicated with the image disc placed at a vertical distance z (along vector v_1 in Fig. 2). An intermolecular potential was then calculated from the Coulombic interaction between the two discs as a function of the horizontal displacement distance d. Permutations of the disc internal parameters (r, α and a) were performed for vertical distances 0.2 Å $< z <$ 35 Å in increments of 0.2 Å , while a was varied between 0.1 e Å^{-2} and 10.0 e Å^{-2} in increments of 0.1 eÅ^{-2}. A complete scan of this variable set was applied to a disc with a radius $r = 10$ Å, with the corona size 1 Å $< \alpha <$ 10 Å.

A typical shape for the electrostatic interaction as a function of the displacement d is shown in Fig. 3, which gives three specific energies:

i) The effective binding energy is taken as the energy gap between the energy minimum and the infinite separation energy at 0 kJ mol^{-1};
ii) The energy barrier to binding is taken as the energy difference between no interaction (0 kJmol^{-1}) and the local maximum;
iii) The absolute maximum energy, seen at $d = 0$, corresponds to the case where two discs lie directly above each other. This is unfavourable from an electrostatic point of view, though, in principle, could become energetically favourable in the presence of strong van der Waal's interactions.

Results and Discussion

a) Effects of interlayer distance z
The inter-molecule distance, z, has a strong effect on the d-dependence of the potential. The latter can be categorized into one of two main types, corresponding to long and short distances of separation. At large z, the d-dependent potential (Fig. 4) starts at a global maximum for zero displacements and then decays to a non-interacting state. At short interlayer distances the molecules show an initial global maximum where the two discs are eclipsed followed by a global energy minimum (below zero) representing a bound state. The global minimum state is

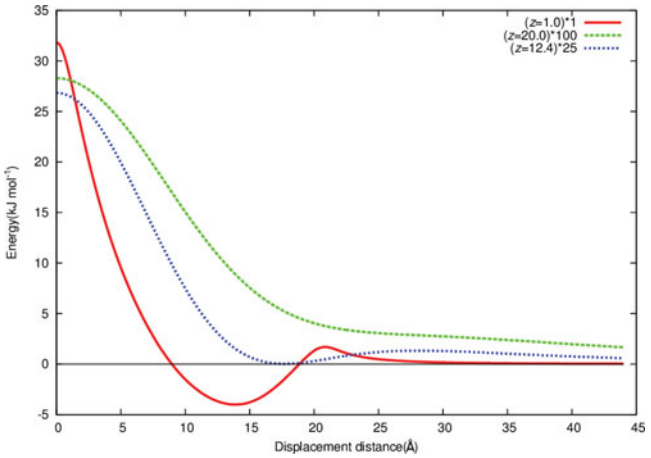

Figure 4. Graph showing how vertical distance of separation, *z,* affects the potential of a disc with a core of 10 Å and a corona of 1 Å, the solid red line is indicative of a small inter-molecule separation (not scaled), the dashed green line is indicative of a large interlayer separation (scaled by a factor of 100) and the dotted blue line is indicative of an intermediate inter-molecule separation (scaled by a factor of 25), with a local bound minimum. The scaling of the potentials is to enable a comparison of the three function shapes.

followed by a local maximum (energy barrier to binding) and a slow decay to no interaction as $d \to \infty$. Between these two extremes exists a small range of interlayer distances where a local minimum exists, which is higher in energy than the non-interacting state.

The energy minimum gives the favourable stacking arrangement for two discs, which can be controlled by the relative size and shape of the core disc and corona. In experimental studies of chromonic aggregation, individual chromonic molecules aggregate into stacks where local stacking is controlled by the strength of this interaction. Here, a local energy maximum is also important, as this helps to stabilise a nematic phase over a biphasic system where the stacks associate and undergo phase separation from the solvent.

The location of the global minimum is strongly z-dependent, only at larger values of z. A disc core of 10 Å with a corona of 1 Å, at a z value of 1.0 Å has a minimum in the d-dependent potential located at a displacement of 13.86 Å. This is an identical displacement to that found for the same disc with a z value within the typical experimental range (3.4 – 3.6 Å). However, at the binding limit of $z = 12.4$ Å the minimum is located at a displacement of 17.6 Å, implying that the potential is only sensitive to z at larger values. Naturally, the z limit of the binding is dependent also on the molecule size (table 1). Experimentally determined, π-π stacking distances are usually quoted at $\approx 3.4 - 3.6$ Å. At shorter distances than this, strongly repulsive molecular interactions dominate the potential, and at larger distances van der Waal's attractions are significantly reduced. So in the further studies below we choose a value of $z = 3.6$ Å as a representative stacking distance for the model chromonics.

b) Influence of the magnitude of charge separation

The effect of increasing the magnitude of charge on the core (and counter charge on the corona) is easy to identify from Fig. 5. Increasing the charge separation has

Table 1. Table of disc models, with the maximum vertical binding distance as the first vertical distance that produces only positive energies (intermediate inter-molecule separation) and extrapolated minimum core sizes. The minimum core size refers to the minimum size of core necessary for favourable binding.

Core:corona ratio	Total disc size / Å	Maximum vertical binding distance / Å	Minimum core size / Å
10:1	11	12.4	2.82
5:1	12	13.2	2.65
10:3	13	13.6	2.57
5:2	14	14.2	2.46
2:1	15	14.8	2.36
5:3	16	15.2	2.30
10:7	17	15.6	2.24
5:4	18	16.2	2.16
10:9	19	16.6	2.11
1:1	20	17.0	2.06

no effect on the position of stationary points or any of the roots of the potential function, but does increase both the effective binding energy and the local maximum. A potential curve calculated for a given core charge can therefore be transformed into the potential for any other charge using a simple scalar.

c) Effects of molecular geometry r and a
The sizes of the core and corona regions have a significantly impact on d-dependence of the potential, influencing both the calculated maximum and minimum (see Fig. 6). At a fixed distance of $z = 3.6$ Å the location of the global minimum can be controlled

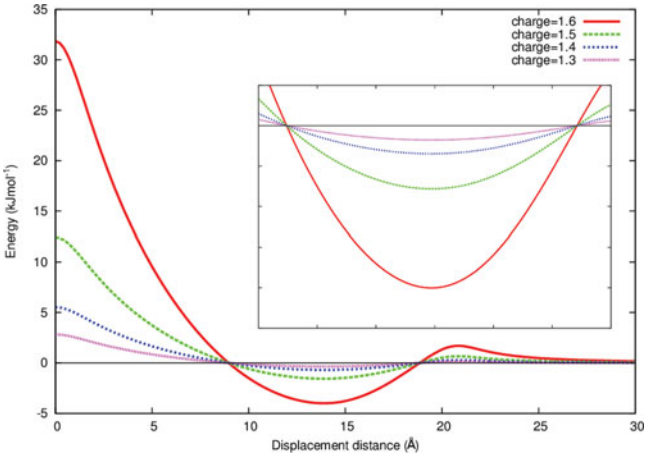

Figure 5. Graph showing the dependence of potential on the magnitude of the charge on the core (and counter charge on the corona) for $z = 3.6$ Å. The inset shows an expanded section of the potential between the two roots. The charge refers to the excess electron present in the core (1e≡1.602×10−19 C).

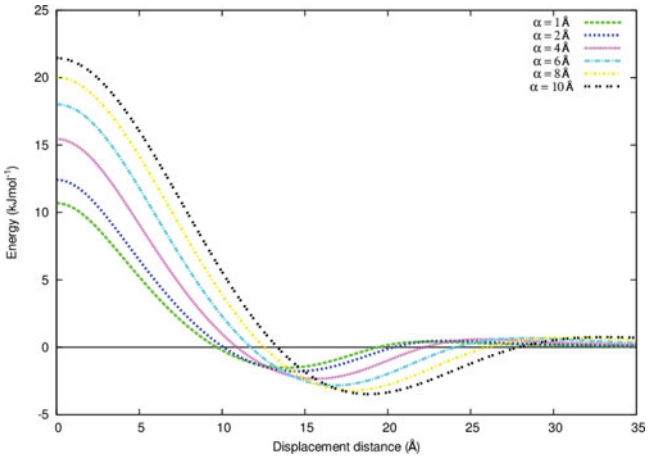

Figure 6. Graph showing the effect on binding potential at a vertical separation of 3.6 Å for a model with a fixed $r = 10$ Å core and corona with 1 Å $< \alpha <$ 10 Å.

by varying either the size of the core or the size of the corona. Figure 7 shows the change in the global minimum by varying the corona size for a fixed core size of 10 Å. The position of the energy minimum can be fitted by the relation 4/3 r + 9/16 α. While we place no physical importance on the 4/3 and 9/16 terms, given they will be dependent on the interlayer distance, we do note that this provides a simple relationship to calculate the ideal displacement distance for a chromonic molecule with particular sizes of core and corona.

Naturally, the minimum energy displacement calculated in this manner represents only the effects of charge separation. Non-uniform van der Waal's interactions could in principle influence separation as could solvent effects. While a full treatment

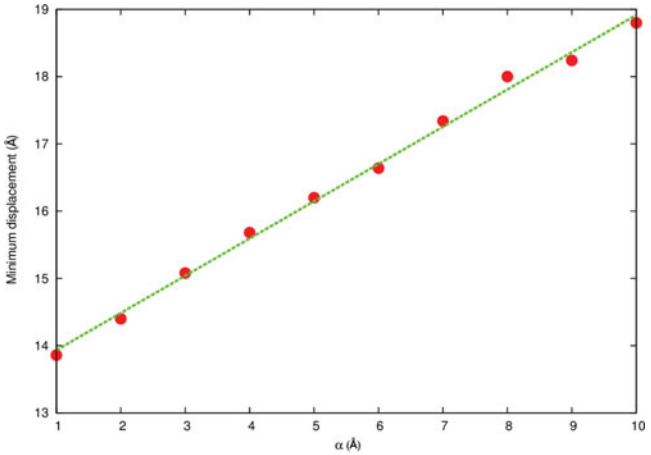

Figure 7. Correlation between the size (10 Å) of the corona (α Å) and the minimum energy displacement, points represent simulation minima, the line represents a line of best fit. Position of the minimum in the binding energy $= 1.34r + 0.557\alpha$ or approximately $(4/3)r + (3/4)^2\alpha$. for short z distances.

of these factors is beyond the scope of the current study, it is possible to make the general comment that to reduce unfavourable hydrophobic effects, the solvent accessible surface area of the aggregate (in this case dimer) should be reduced. In all cases this can be accommodated by reducing the displacement distance d. Hence we expect the hydrophobic effect to reduce the position of the minimum displacement.

d) Minimum size for a chromonic mesogen
Given that there is an inter-molecule distance, z, above which no bound configuration occurs, and that reducing the core size is equivalent to decreasing the distance at which this condition is met; we can infer that there is a minimum core size ($r_{\min}$) that still gives a bound configuration at $z = 3.5$ Å. The minimum core size for each model is given in table 1. Using a linear extrapolation, a single phenyl ring of core size $r = 1$ Å would require a corona of at least $\alpha = 22$ Å to provide a bound configuration. While this is not completely infeasible, branched functional groups would be necessary to fully fill the corona around the phenyl ring to a distance of 22 Å. These would almost certainly fill configurational space out of plane of the ring, reducing the disc-like nature of the molecule and hence eliminating any chromonic behaviour.

Conclusions

Charge based contributions to chromonic aggregation have been studied using a simple core-corona model which reproduces the expected binding profile for chromonic molecules. The size of the binding potential can be increased by increasing the size of the charge separation between core and corona. Changing vertical separation between discs gives rise to two forms for the d-dependent potential. At short separations the potential has an attractive minimum, which favours a bound molecule. Additionally, the presence of a local maximum in this potential, contributes to the stabilization of chromonic molecules in stacks, i.e. helps prevent phase segregate by providing an energy cost associated with the aggregation of multiple stacks. At large distances the potential is purely repulsive and favours an unbound state. The size of the core and corona affect the potential subtly by shifting the position of the minimum and local maximum.

The relationship between the size of the cores, the interlayer distance and the potential function, allows a theoretical minimum size to be determined for the core of a model commensurate with a stacking of 3.5 Å. This helps to explain why no chromonic phases have been observed for small core molecules such as a substituted phenyl ring.

References

[1] Lydon, J., (1998). Curr. Opin. *Colloid Interface Sci.*, *3*, 458.
[2] Edwards, D. J., Jones, J. W., Lozman, O., Ormerod, A. P., Sintyureva, M. & Tiddy, G. J. T., (2008). *J. Phys Chem. B*, *112*, 14628
[3] Mills, E. A., Regan, M. H., Stanic, V., & Collings, P. J., (2012). *J. Phys. Chem. B*, *116* (45), 13506.
[4] Tiddy, G. J. T., Mateer, D. L., Ormerod, A. P., Harrison, W. J., & Edwards, D. J. (1995). *Langmuir*, *11*, 390.
[5] Lydon, J.,(2010). *J. Mater Chem.*, *20*, 10071.
[6] Walker, M., Masters, A. J., & Wilson, M. R., (2014). *Phys. Chem. Chem. Phys.* DOI: 10.1039/c4cp03092c
[7] Cox, J. S., Woodard, G. D., & McCrone, W. C., (1971). *J. Pharm. Sci.*, *60*, 1458.

[8] Lu, W., Chen, Y., Roy, V. A. L., Chui, S. S. Y., & Che, C. M., (2009). *Angew. Chem. Int. ed.*, *48*, 7621.
[9] Chami, F., & Wilson, M. R., (2010). *J. Am. Chem. Soc.*, *132*(22), 7794.
[10] Boden, N., Bushby, R. J., Ferris, L., Hardy, C., & Sixl, F., (1986). *Liq. Cryst.*, *1*, 109.
[11] Al-Lawati, Z. H., Alkhairalla, B., Bramble, J. P., Henderson, J. R., Bushby, R. J., & S. D. Evans, S. D., (2012). *J. Phys. Chem. C*, *116*, 12627.
[12] Hughes, R. E., Hart, S. P., Smith, D. A., Movaghar, B., Bushby, R. J., & Boden, N., (2002) *J. Phys. Chem. B*, *106*, 6638.
[13] Lerman. L. S., (1961). *J. Mol. Biol.*, *3*, 18.
[14] Sinnikrot, M. I., & Sherrill, C. D., (2004). *J. Phys. Chem. A*, *108*, 10200.
[15] Hill, J. G., Platts, J. A., & Werner, H.,(2006). *Phys. Chem. Chem. Phys.*, *8*, 4072.
[16] Hunter, C. A., & Sanders, J. K. M., (1990). *J. Am. Chem. Soc.*, *112*, 5525.
[17] Hohenstein, E. G., Duan, J. N., & Sherrill, C. D., (2011). *J. Am. Chem. Soc.*, *133*, 13244.