Controlling the Local Arrangement of Polycyclic Aromatic Hydrocarbons through Substituent Effects in π-Stacking Interactions

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A conceptual model of substituent effects in π-stacking interactions between aromatic systems will be presented that depends only on local, direct interactions between the substituents and the other arene. This model is drastically different than conventional views of π-stacking, which hinge upon substituent-induced changes of the π-system of the substituted ring. This local, direct interaction model yields unambiguous predictions regarding substituent effects in myriad stacking interactions, including polysubstituted and heterocyclic systems. Moreover, these predictions are in full accord with robust *ab initio* and DFT computations, and provide a simple means of understanding substituent effects in complex stacked dimers. Overall, this new view of π-stacking interactions predicts that substituent effects will be additive, transferable, and dependent on the relative orientation of interacting arenes.

The utility of this view of substituent effects in π-stacking interactions will be demonstrated in applications of DFT to large π-stacked polycyclic aromatic systems. In particular, we will demonstrate that the local orientation of discotic liquid crystal materials can be controlled through substituent effects. Such control over the local arrangement of stacked systems should provide an approach to maximize charge-transfer rates in discotic liquid crystals.