Theoretical Study of the Remote Control of Hydrogen Bond Strengths in Donor–Bridge–Acceptor Systems: Principles for Designing Effective Bridges with Substituent Tuning

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Abstract: Remote control of hydrogen bond strengths has been studied based on conjugated donor–bridge–acceptor (pyrrole–bridge–imine) systems. The neutral and protonated states of the imine can change the hydrogen bonding ability of the pyrrole because, in the protonated state, significant partial intramolecular charge transfer (ICT) is induced that causes partial delocalization of the positive charge onto the pyrrole moiety. An efficient bridge, regardless of its length, should help electrons to flow out of pyrrole. A previously developed design strategy for the bridge (low bridge HOMO/LUMO) leads to the study of cyano- and fluoro-substituted conjugated systems. Substitution positions are found to be of key importance for maximizing the protonation-induced response from the donor–bridge–acceptor systems. Our results not only help to identify useful bridge substitution patterns, but also highlight interesting issues regarding the bridge conformation and the fluorine lone-pair effect.

Keywords: density functional calculations · electronic structure · hydrogen bonding · intramolecular charge transfer · supramolecular chemistry

Introduction

Supramolecular chemistry and self-assembly have the potential to play important roles in the construction of functional materials.[1] A core feature of supramolecular chemistry and self-assembly is noncovalent synthesis, and one of the frequently used interactions in noncovalent synthesis is hydrogen bonding.[2] In recent experimental studies, strength or binding orientation of hydrogen bonds have been manipulated by changing the charge state of the system by reactions such as protonation, oxidation/reduction, metal coordination, or chemical transformation.[3–5] The implication of these studies is that chemists can use external stimuli to design versatile materials which are responsive to the environment. In view of the importance of hydrogen bonding in noncovalent synthesis and the potential usage of binding manipulation, we have carried out theoretical calculations to formulate guidelines for the design of binding systems that can be controlled effectively by external stimuli. Because functional materials of different lengths (sizes) may be desired, in our theoretical studies, we paid much attention to the issue of how to design systems that are able to maintain their responses toward an external stimulus, regardless of the size of the molecules.[6]

To study the length effect, the systems we study must contain three conceptual parts: a hydrogen-bonding center, a reaction center for the stimulus, and a bridge whose length can be varied. In our previous investigations, we controlled the hydrogen-bonding ability of pyrrole by the protonation of a remote imine reaction center that was covalently linked to the pyrrole by a π-conjugated bridge.[6] (The molecular framework was represented as pyrrole–$(X=X)_n$–imine; examples of X will be given later.) Because pyrrole is electron-rich and imine is electron-poor, the three-component systems can be classified as donor–bridge–acceptor (D–B–A) molecules. The D–B–A type molecules are well known for their nonlinear optical properties;[7] however, the binding properties of these molecules are less well studied. When protonation took place in pyrrole–$(X=X)_n$–imine, the iminium center acted as a strong electron acceptor and triggered a push–pull process from the electron donor (pyrrole) site. The consequence of partial intramolecular charge transfer (ICT) between the electron-donor and the electron-acceptor

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sites was that the positive charge brought in by the proton was partially delocalized onto the pyrrole, as well as onto other parts of the conjugated molecule (Scheme 1). As a
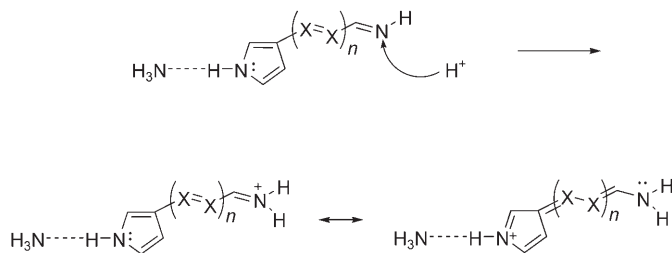
Scheme 1. Protonation of pyrrole-$(X=X)_n$-imine induces ICT. Ammonia is used as a binding partner for the three-component system.

result, the hydrogen-bonding ability of the pyrrole was enhanced relative to the unprotonated system. Effectively, a chemical signal input (protonation) has been transformed into a physical output (binding change) in such systems and, therefore, the three-component systems can be regarded as signal transducers (Figure 1).
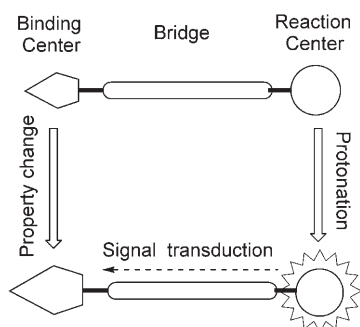

Figure 1. Protonation-induced binding change in the three-component system.

According to conventional knowledge of the substituent effect, the electron-withdrawing power of iminium should have less effect on pyrrole as the length of the bridge increases. This was indeed the case in the pyrrole–$(CH=CH)_n$–imine systems; as the bridge became longer, protonation of imine caused a smaller binding change (i.e. weaker signal transduction). However, it was found that long azo bridges provided good signal maintenance in our three-component systems.[6a] Systematic studies of protonated three-component systems with hybrid bridges containing C and N atoms lead to a simple working model to rationalize the calculated re-

sults: an electron was donated from the HOMO of pyrrole to the *combined* LUMO of the other two components, the bridge-iminium moiety (Figure 2). The combined LUMO of the bridge-iminium moiety was in turn determined by the frontier orbitals of the bridge and the very low-lying empty orbital of iminium. The π-HOMO of $(CH=CH)_n$ bridges were high-lying so that the low-lying LUMO of iminium not only interacted with the bridge π-LUMO, but also with the π-HOMO (see inset in Figure 2). As the bridge became longer, the bridge π-HOMO increased in energy owing to more extensive conjugation. If the LUMO of the iminium interacted with the bridge π-HOMO more than with the bridge π-LUMO, which was the case for pyrrole–$(C=C)_n$–iminium, the resultant two-component LUMO followed the trend of the bridge π-HOMO. That is, under the influence of the bridge π-HOMO, the two-component LUMO increased in energy as the length of the bridge increased, which resulted in a decrease in the extent of electron donation from the pyrrole. The $(N=N)_n$ bridges had low-lying π-HOMO orbitals, so the LUMO of iminium interacted primarily with the bridge π-LUMO, and the resultant two-component LUMO energy decreased as the bridge lengthened. With this simple model, it became clear that the low-lying π-HOMO and π-LUMO of the azo bridges were beneficial for remote protonation-induced ICT.[6b] As it is difficult to synthesize purely nitrogen-based π-conjugated bridges, in this article, we explore the possibility of achieving signal-maintaining effects with substituted carbon-based bridges.

Substituent effects[8] are known to influence molecular properties. In π-conjugated materials, substituents have been added to carbon-based conjugated molecules to promote the desired optical and electrical properties.[9–13] For example, perfluorinated phenylenes and cyano-containing phenylene-vinylene-type polymers (e.g. CN-PPV) have been synthesized to improve the electron affinity of conjugated polymers. They are used in OLED (organic light-emitting diodes) to improve electron injection.[9,10,13a,b] Cyano-containing terthiophene-based quinodimethane has been found to be an *n*-channel conductor in a thin film transistor while most organic semiconductors exhibited *p*-channel conductivity.[12] The influence of substituent effects on hydrogen-bonded complexes is also well documented.[14–15] Previously, we have tested the notion that bridges with low-lying π-
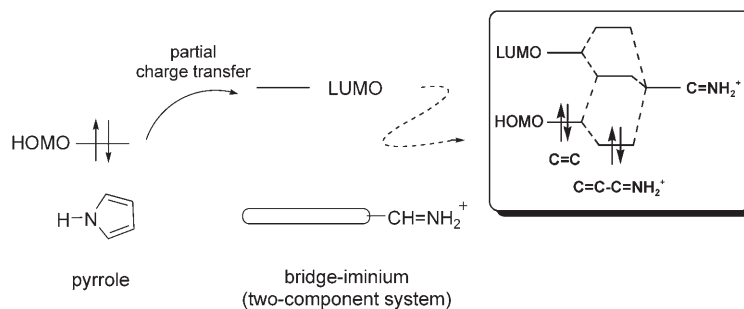

Figure 2. Model to rationalize partial ICT in the three-component systems. The inset shows that the two-component LUMO is determined by frontier orbitals of the bridge and the LUMO of the reaction center.

HOMO and π-LUMO could be beneficial for charge transfer with three-component systems bearing $(CH=CH)_n$ and $(CF=CF)_n$ bridges.[6b] The cyano group is more electron-withdrawing than the fluoro group. It is of interest to find out whether the cyano group is indeed superior to the fluoro group as implied by our rationalization model. Furthermore, it is known that the positions of electron-withdrawing/donating moieties influence the nonlinear optical properties in conjugated donor–bridge–acceptor (D–B–A) systems.[7g,h] Therefore, both electronic and position effects of fluoro and cyano substituents are investigated in this study. In the first part of the Results and Discussion, we compare pyrrole–$(CH=CH)_n$–imine, pyrrole–$(CF=CF)_n$–imine, pyrrole–$(C(CN)=C(CN))_n$–imine, and pyrrole–$(N=N)_n$–imine systems in terms of superiority in maintenance of signal transduction. The effects of different theory levels and basis sets are also described. In the second part, unsymmetrically substituted systems of pyrrole–$(CR^1=CR^2)_n$–imine ($n = 1–4$, $R^1 = CN$, F, $R^2 = H$; $R^1 = H$, $R^2 = CN$, F), and pyrrole–$(CR^1=CR^1–CR^2=CR^2)_n$–imine ($n = 1–2$; $R^1 = CN$, F, $R^2 = H$; $R^1 = H$, $R^2 = CN$, F) are compared to the systems with fully substituted bridges. Our results not only help to identify useful bridge substitution patterns, but also highlight interesting issues with regard to bridge conformation and the fluorine lone-pair effect. It should also be emphasized that while the bridge effects on the photophysics of D–B–A systems[16,17] have been widely studied, the bridge effects on binding modulation have received far less attention.[6,18] Therefore, theoretical studies can play an important role in guiding molecular design.

Computational Details

All calculations were performed by Gaussian 98 and Gaussian 03 programs.[19] The geometries of the three-component systems were fully optimized, and frequency analyses were carried out to verify that structures were minima on the potential energy surface. As in previous studies, ammonia was used to probe the binding ability of a three-component system.[6] The binding energy (ΔE_b) was corrected via the counterpoise (CP) correction for the basis set superposition error.[20] Calculations with 6-31G(d), 6-31+G(d), 6-31+G-(d,p), and 6-31+G(2d,2p) basis sets at the HF and higher theory levels (MP2, DFT) were carried out on selected three-component systems to compare them with the calculated trends of binding energies. As the trend calculated at the HF/6-31G* level was found to be the same as the results calculated at higher levels, all results in the second part of the Results and Discussions were calculated at the HF/6-31G* level. Qualitative trends of frontier orbitals of the bridges were approximated with HF/6-31G*-optimized H–$(CR^1=CR^2)_n$–H and H–$(CR^1=CR^1–CR^2=CR^2)_n$–H molecules.

Results and Discussion

Three-component systems with $(CH=CH)_n$, $(CF=CF)_n$, $(C(CN)=C(CN))_n$, and $(N=N)_n$ bridges: Ammonia binding energies of three-component systems in the neutral and protonated states ($\Delta E_{b(N)}$ and $\Delta E_{b(P)}$, respectively) are listed in Table 1. Two properties of the three-component systems are

Table 1. Binding energies [kcal mol^{-1}] and binding energy differences between protonated and neutral three-component systems with different bridges calculated at the HF/6-31G(d) level.

Bridge		$n = 1$	$n = 2$
$(CH=CH)_n$[a]	$\Delta E_{b(N)}$	−6.57	−6.55
	$\Delta E_{b(P)}$	−13.17	−12.03
	$\Delta\Delta E_{b(P-N)}$	**−6.60**	**−5.48**
$(CF=CF)_n$	$\Delta E_{b(N)}$	−7.07	−7.27
	$\Delta E_{b(P)}$	−14.00	−13.31
	$\Delta\Delta E_{b(P-N)}$	**−6.93**	**−6.04**
$(C(CN)=C(CN))_n$	$\Delta E_{b(N)}$	−8.19	−8.79
	$\Delta E_{b(P)}$	−15.60	−16.15
	$\Delta\Delta E_{b(P-N)}$	**−7.41**	**−7.36**
$(N=N)_n$[a]	$\Delta E_{b(N)}$	−7.11	−7.46
	$\Delta E_{b(P)}$	−15.50	−16.46
	$\Delta\Delta E_{b(P-N)}$	**−8.39**	**−9.00**

[a] The values of $\Delta E_{b(N)}$ are slightly different from those reported in reference [6], namely, by no more than 0.3 kcal mol^{-1}. As a result, $\Delta\Delta E_{b(P-N)}$ values are also slightly different from those in reference [6]. The differences arise from different N–H configurations of imine. As shown in Scheme 1, the N–H bond is *trans* to the (X=X) moiety in this study. The *cis* N-H configuration was studied in reference [6]. No reversal of trend was found because the energy difference is small.

of central importance: signal sensitivity and signal maintenance. Good signal sensitivity is represented by a large difference between the binding energies of the neutral and protonated states, $\Delta\Delta E_{b(P-N)}$, and good signal maintenance is reflected by small differences between $\Delta\Delta E_{b(P-N)}$ in a series of three-component systems with different bridge lengths. Table 1 shows that, among the three carbon-based bridges, three-component systems with $(C(CN)=C(CN))_n$ afford the largest $\Delta\Delta E_{b(P-N)}$ values and the smallest difference in $\Delta\Delta E_{b(P-N)}$ from $n = 1$ to 2. Therefore, as expected, the strong substituent effect of CN has made these vinyl systems superior in terms of signal sensitivity and maintenance compared to the unsubstituted or fluorinated systems. When systems with azo bridges are also considered, the order of bridge superiority in signal transduction is $(N=N)_n > (C(CN)=C(CN))_n > (CF=CF)_n > (CH=CH)_n$.

The trend of signal sensitivity and maintenance observed in Table 1 ($(N=N)_n$ systems > $(C(CN)=C(CN))_n$ systems > $(CH=CH)_n$ systems) was validated with more calculations at different levels of theory (HF, B3LYP, MP2, MP4) with various basis sets (6-31G(d), 6-31+G(d), 6-31+G(d,p), and 6-31+G(2d,2p)). No reversal of trend has been observed from the fully optimized calculations, so only results with the smallest and largest basis sets are shown in Table 2. It was found that, at a given level of theory, the bridge length effects were similar, regardless of the size of the basis set. For example, as the bridge length increased, the sensitivity

Table 2. Binding energies [kcal mol^{-1}] and binding energy differences between protonated and neutral three-component systems at different levels of theory and with different basis sets.

Bridge		(CH=CH)$_n$		(C(CN)=C(CN))$_n$		(N=N)$_n$	
		$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
HF/6-31G(d)	$\Delta E_{b(N)}$	−6.57	−6.55	−8.19	−8.79	−7.11	−7.46
	$\Delta E_{b(P)}$	−13.17	−12.03	−15.60	−16.15	−15.50	−16.46
	$\Delta\Delta E_{b(P-N)}$	**−6.60**	**−5.48**	**−7.41**	**−7.36**	**−8.39**	**−9.00**
HF/6-31+G(2d,2p)	$\Delta E_{b(N)}$	−5.19	−5.17	−6.55	−7.02	−5.63	−5.91
	$\Delta E_{b(P)}$	−10.83	−9.85	−13.05	−13.51	−12.94	−13.90
	$\Delta\Delta E_{b(P-N)}$	**−5.64**	**−4.68**	**−6.50**	**−6.49**	**−7.31**	**−7.99**
B3LYP/6-31G(d)	$\Delta E_{b(N)}$	−8.96	−9.03	−10.94	−11.77	−9.84	−10.52
	$\Delta E_{b(P)}$	−17.03	−15.84	−19.46	−19.48	−19.30	−19.49
	$\Delta\Delta E_{b(P-N)}$	**−8.07**	**−6.81**	**−8.52**	**−7.71**	**−9.46**	**−8.97**
B3LYP/6-31+G(2d,2p)	$\Delta E_{b(N)}$	−6.65	−6.68	−8.29	−8.93	−7.42	−7.97
	$\Delta E_{b(P)}$	−13.39	−12.34	−15.62	−15.62	−15.45	−15.64
	$\Delta\Delta E_{b(P-N)}$	**−6.74**	**−5.66**	**−7.33**	**−6.69**	**−8.03**	**−7.67**
MP2/6-31G(d)[a]	$\Delta E_{b(N)}$	−8.58	−8.59	−10.42	−11.20	−9.35	−9.84
	$\Delta E_{b(P)}$	−16.24	−15.06	−18.68	−18.76	−18.72	−19.27
	$\Delta\Delta E_{b(P-N)}$	**−7.66**	**−6.47**	**−8.26**	**−7.56**	**−9.37**	**−9.43**
MP2/6-31+G(2d,2p)[a]	$\Delta E_{b(N)}$	−7.28	−7.28	−8.84		−7.94	−8.35
	$\Delta E_{b(P)}$	−13.85	−12.81	−16.03		−16.09	−16.58
	$\Delta\Delta E_{b(P-N)}$	**−6.57**	**−5.53**	**−7.19**		**−8.15**	**−8.23**
MP2/6-31+G(2d,2p)//HF/6-31G(d)	$\Delta E_{b(N)}$	−7.26	−7.25	−8.82	−9.38	−7.88	−8.28
	$\Delta E_{b(P)}$	−13.66	−12.69	−15.71	−14.34	−15.65	−15.56
	$\Delta\Delta E_{b(P-N)}$	**−6.40**	**−5.44**	**−6.89**	**−4.96**	**−7.77**	**−7.28**
MP2/6-31+G(2d,2p)//B3LYP/6-31G(d)	$\Delta E_{b(N)}$	−7.24	−7.23	−8.81	−9.45	−7.90	−8.29
	$\Delta E_{b(P)}$	−13.85	−12.80	−16.07	−16.08	−16.13	−16.67
	$\Delta\Delta E_{b(P-N)}$	**−6.61**	**−5.57**	**−7.26**	**−6.63**	**−8.23**	**−8.38**
MP2/6-31+G(2d,2p)//B3LYP/6-31+G-(2d,2p)	$\Delta E_{b(N)}$	−7.33	−7.35	−8.89	−9.50	−7.99	−8.39
	$\Delta E_{b(P)}$	−13.89	−12.87	−16.10	−16.10	−16.14	−16.64
	$\Delta\Delta E_{b(P-N)}$	**−6.56**	**−5.52**	**−7.21**	**−6.60**	**−8.15**	**−8.25**
MP4/6-31G(d)//B3LYP/6-31G(d)	$\Delta E_{b(N)}$	−7.35	−7.28	−9.02	−9.58	−7.92	−8.17
	$\Delta E_{b(P)}$	−14.72	−13.55	−17.25	−17.59	−17.42	−18.31
	$\Delta\Delta E_{b(P-N)}$	**−7.37**	**−6.27**	**−8.23**	**−8.07**	**−9.50**	**−10.14**

[a] Frequency analysis was not performed owing to limited computing resources.

of the (CH=CH)$_n$ systems decreased by about 1 kcal mol^{-1} both at the HF/6-31G(d) and HF/6-31+G(2d,2p) levels. For the (C(CN)=C(CN))$_n$ systems, both basis sets maintained the level of sensitivity; for the (N=N)$_n$ systems, sensitivity increased by about 0.6 kcal mol^{-1}. The three-component system with (C(CN)=C(CN))$_2$ was not optimized at the MP2 level with basis sets larger than 6-31G(d) owing to limited computing resources. Nevertheless, because the binding energies calculated with MP2/6-31+G(2d,2p)//B3LYP/6-31+G(2d,2p) were almost identical to that calculated with MP2/6-31+G(2d,2p), the above trends in the signal sensitivity and maintenance can almost be regarded as confirmed at the MP2/6-31+G(2d,2p) level. At the MP4 level, only single-point calculations were carried out (MP4/6-31G(d)//B3LYP/6-31G(d)). The bridge length effects are signal reducing, maintaining, and amplifying in the (CH=CH)$_n$, (C(CN)=C(CN))$_n$, and (N=N)$_n$ systems, respectively. It is noted that geometries at the B3LYP and MP2 levels are more similar than at the HF level, so that the binding results at the MP2/6-31+G(2d,2p)//B3LYP/6-31G(d) level are rather close to those with MP2/6-31+G(2d,2p), whereas MP2/6-31+G(2d,2p)//HF/6-31G(d) are not. The main difference comes from the protonated species. Therefore, protonated π-conjugated structures at the HF level may not always be compatible with higher level single-point calculations.

Judged by $\Delta\Delta E_{b(P-N)}$ of different bridge lengths, one would classify the (N=N)$_n$ bridges as signal amplifying at the HF and MP4 levels, signal reducing at the B3LYP level, and slightly signal amplifying (or signal maintaining) at the MP2 level. The (C(CN)=C(CN))$_n$ bridge is signal maintaining at the HF and MP4 levels, signal reducing at the B3LYP and MP2 levels. Because, in reality, the solvent or the counterion will affect the signal transduction performance of a three-component system, we feel it is unnecessary to pursue whether a bridge is truly signal-maintaining or amplifying by means of calculations at a higher level of theory. Our ultimate goal is to find principles for designing efficient three-component systems in which a stimulus-induced response can be maximized. As long as a qualitative trend can be rationalized on the basis of a sound chemical concept and this leads to rational molecular design, theoretical calculations have served their purpose. As the relative bridge efficiency in signal transduction predicted by all levels are the same, in the following sections, HF/6-31G(d) is used to probe the trends of signal communication. In those cases in which a confirmation of a trend is needed, calculations at a higher theory level are also performed.

We have already demonstrated that insertion of a N=N unit into the repeating unit of a bridge, ((CH=CH)$_n$–N=N), dramatically improves the signal maintenance of carbon bridges.[6a] Because a (C(CN)=C(CN))$_n$ bridge is significantly better than a (CH=CH)$_n$ bridge, it is of interest to find out whether the C(CN)=C(CN) unit can generate a similar effect as with N=N insertion. Table 3 presents the calculated binding energies of three-component systems with ((CH=CH)$_n$–C(CN)=C(CN))$_x$ bridges, where $n = 1–4$, $x = 1–2$. It can be seen that these bridges do not result in significant signal reduction as for pure carbon bridges ($\Delta\Delta E_{b(P-N)}$ of three-component systems with (CH=CH)$_n$ ($n = 1–4$) decreased by more than 2 kcal mol^{-1}[6a]). Therefore, the C(CN)=C(CN) unit can greatly improve the signal reduction effect of a pure carbon bridge just as with an azo unit. The role of N=N and C(CN)=C(CN) in hybrid bridges will be discussed in a separate report, in which heteroaromatic and phenyl rings are studied, and will not be discussed further here.

Table 3. Binding energies [kcal mol^{-1}] and binding energy differences between protonated and neutral three-component systems with ((CH=CH)$_n$–C(CN)=C(CN))$_x$ at the HF/6-31G(d) level.

Bridge		$x = 1$	$x = 2$
((CH=CH)$_1$–C(CN)=C(CN))$_x$	$\Delta E_{b(N)}$	−7.54	−7.80
	$\Delta E_{b(P)}$	−14.66	−15.26
	$\Delta\Delta E_{b(P-N)}$	**−7.12**	**−7.46**
((CH=CH)$_2$–C(CN)=C(CN))$_x$	$\Delta E_{b(N)}$	−7.20	−7.26
	$\Delta E_{b(P)}$	−14.04	−14.61
	$\Delta\Delta E_{b(P-N)}$	**−6.84**	**−7.35**
((CH=CH)$_3$–C(CN)=C(CN))$_x$	$\Delta E_{b(N)}$	−6.96	−6.93
	$\Delta E_{b(P)}$	−13.49	−13.91
	$\Delta\Delta E_{b(P-N)}$	**−6.53**	**−6.98**
((CH=CH)$_4$–C(CN)=C(CN))$_x$	$\Delta E_{b(N)}$	−6.79	−6.74
	$\Delta E_{b(P)}$	−12.98	−13.31
	$\Delta\Delta E_{b(P-N)}$	**−6.19**	**−6.57**

Table 4. Binding energies [kcal mol^{-1}] and binding energy differences between protonated and neutral three-component systems with different bridges.

Bridge		$n = 1$	$n = 2$	$n = 3$	$n = 4$
(C(CN)=C(CN))$_n$	$\Delta E_{b(N)}$	−8.19	−8.79	−9.08	−9.20
	$\Delta E_{b(P)}$	−15.60	−16.15	−20.00	−20.40
	$\Delta\Delta E_{b(P-N)}$	**−7.41**	**−7.36**	**−10.92**	**−11.20**
(C(CN)=CH)$_n$	$\Delta E_{b(N)}$	−7.31	−7.54	−7.66	−7.72
	$\Delta E_{b(P)}$	−14.17	−13.37	−12.46	−11.23
	$\Delta\Delta E_{b(P-N)}$	**−6.86**	**−5.83**	**−4.80**	**−3.51**
(CH=C(CN))$_n$	$\Delta E_{b(N)}$	−7.53	−8.13	−8.52	−8.76
	$\Delta E_{b(P)}$	−14.44	−14.16	−13.99	−13.92
	$\Delta\Delta E_{b(P-N)}$	**−6.91**	**−6.03**	**−5.47**	**−5.16**
(C(CN)=C(CN)−CH=CH)$_n$	$\Delta E_{b(N)}$	−8.06	−8.47		
	$\Delta E_{b(P)}$	−13.60	−12.31		
	$\Delta\Delta E_{b(P-N)}$	**−5.54**	**−3.84**		
(CH=CH−C(CN)=C(CN))$_n$	$\Delta E_{b(N)}$	−7.54	−7.80		
	$\Delta E_{b(P)}$	−14.66	−15.26		
	$\Delta\Delta E_{b(P-N)}$	**−7.12**	**−7.46**		
(CF=CF)$_n$	$\Delta E_{b(N)}$	−7.07	−7.27	−7.38	−7.54
	$\Delta E_{b(P)}$	−14.00	−13.31	−12.82	−12.51
	$\Delta\Delta E_{b(P-N)}$	**−6.93**	**−6.04**	**−5.44**	**−4.97**
(CF=CH)$_n$	$\Delta E_{b(N)}$	−7.07	−7.35	−7.52	−7.65
	$\Delta E_{b(P)}$	−13.26	−12.62	−11.93	−11.39
	$\Delta\Delta E_{b(P-N)}$	**−6.19**	**−5.27**	**−4.41**	**−3.74**
(CH=CF)$_n$	$\Delta E_{b(N)}$	−6.56	−6.47	−6.37	−6.29
	$\Delta E_{b(P)}$	−13.48	−12.62	−11.98	−11.48
	$\Delta\Delta E_{b(P-N)}$	**−6.92**	**−6.15**	**−5.61**	**−5.19**
(CF=CF−CH=CH)$_n$	$\Delta E_{b(N)}$	−7.00	−7.09		
	$\Delta E_{b(P)}$	−12.63	−11.41		
	$\Delta\Delta E_{b(P-N)}$	**−5.63**	**−4.32**		
(CH=CH−CF=CF)$_n$	$\Delta E_{b(N)}$	−6.85	−6.90		
	$\Delta E_{b(P)}$	−12.91	−12.35		
	$\Delta\Delta E_{b(P-N)}$	**−6.06**	**−5.45**		

(CR=CR)$_n$, (CR^1=CR^2)$_n$, and (CR^1=CR^1−CR^2=CR^2)$_n$ bridges: In this section, we consider both fully substituted systems (pyrrole–(CR=CR)$_n$–imine, n = 1–4; R = CN, F) and unsymmetrically substituted systems (pyrrole–(CR^1=CR^2)$_n$–imine, n = 1–4, R^1 = CN, F, R^2 = H; R^1 = H, R^2 = CN, F and pyrrole–(CR^1=CR^1−CR^2=CR^2)$_n$–imine, n = 1–2; R^1 = CN, F, R^2 = H; R^1 = H, R^2 = CN, F). We have already pointed out that the addition of electron-withdrawing groups to a bridge enhances ICT in the protonated three-component systems and thus provides a possible means to improve signal transduction. One would presume that the larger the number of substituents on a bridge, the greater the extent of protonation-induced ICT and hence the higher the $\Delta E_{b(P)}$. Table 4 shows that, for a given bridge length, $\Delta E_{b(P)}$ of fully substituted (CR=CR)$_n$ systems are indeed larger than those of the less substituted (e.g. compare $\Delta E_{b(P)}$ of (C(CN)=C(CN))$_2$, (C(CN)=CH)$_2$, (CH=C(CN))$_2$, (C(CN)=C(CN)−CH=CH)$_1$, and (C(CN)=C(CN)−CH=C(CN))$_1$). Nevertheless, the number and position of substituents also affect $\Delta E_{b(N)}$. As signal sensitivity and maintenance are affected by both $\Delta E_{b(P)}$ and $\Delta E_{b(N)}$, full substitution may not guarantee the best bridge performance. For example, while (C(CN)=C(CN))$_n$ is the best bridge among cyano bridges, (CF=CF)$_n$ is not the best among fluoro bridges. This is because, although $\Delta E_{b(P)}$ of (CH=CH−CF=CF)$_n$ and (CH=CF)$_n$ are somewhat smaller than those of fully substituted (CF=CF)$_n$ systems, their $\Delta E_{b(N)}$ are significantly smaller than those of (CF=CF)$_n$, so that larger binding differences between neutral and protonated states can be achieved with these unsymmetrically substituted bridges. Overall, the superiority in maintenance of signal transduction ($\Delta\Delta E_{b(P-N)}$) with increasing bridge length is as follows: (C(CN)=C(CN))$_n$ > (CH=CH−C(CN)=C(CN))$_n$ > (CH=C(CN))$_n$ > (C(CN)=C(CN)−CH=CH)$_n$ > (C(CN)=CH)$_n$ for cyano-substituted systems and (CH=CH−CF=CF)$_n$ > (CH=CF)$_n$ > (CF=CF)$_n$ > (CF=CF−CH=CH)$_n$ > (CF=CH)$_n$ for fluoro-substituted systems. With the same number of substituents, the best fluoro bridges, (CH=CH−CF=CF)$_n$ (n = 1, 2), are even superior to the (CH=C(CN))$_n$ (n = 2, 4) cyano bridges (see Table 4 for values of $\Delta\Delta E_{b(P-N)}$). Compared to the pure carbon bridge ($\Delta\Delta E_{b(P-N)}$ = −5.31 and −3.90 kcal mol^{-1} for (CH=CH)$_n$, n = 2 and 4, respectively),[6] the $\Delta\Delta E_{b(P-N)}$ values of (CH=CH−CF=CF)$_n$ (n = 1 and 2), −6.06 and −5.45 kcal mol^{-1}, are impressive. Therefore, as long as the substituted positions are carefully planned, a substituent with a weak electronic effect can significantly affect the bridge efficiency in signal transduction.

From a quick glimpse at the results, it is easy to conclude that substitution at the rear positions of unsymmetrical bridges (R^2; the positions closer to the reaction center in a repeating unit are termed the rear positions) are less signal reducing than the substituent at the front (R^1). Interestingly, the origins of this phenomenon are different for the cyano and fluoro systems. We will first comment on cyano systems: when a strong electron-withdrawing group, such as a cyano group, is substituted onto the rear position of (CR^1=CR^2)$_n$, both $\Delta E_{b(N)}$ and $\Delta E_{b(P)}$ are larger than the corresponding values of systems substituted at the front position. This can be rationalized by the fact that, when pyrrole donates its electrons to the rest of the molecule, electron density is accumulated at the rear position, as shown in the resonance form presented in Scheme 2. Therefore, an electron-withdrawing
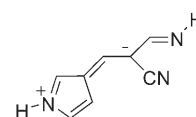
Scheme 2. Resonance structure with electron donation from the pyrrole moiety.

group at the rear position withdraws electrons out of the pyrrole more effectively than at the front position, and hence provides the pyrrole with a stronger binding ability. Aside from this argument based on the resonance effect, we also find an argument based on bridge-dipole moments which is valuable for the understanding of the binding differences caused by the substitution positions. For example, in a simple molecule such as H−$(C(CN)=CH)_n$−H, the electron distribution is shifted toward the CN end owing to its strong electron-withdrawing power. When the electron-withdrawing iminium center is added to the unsubstituted end of the C(CN)=CH bond, the CN group at the other end would counteract the electron-withdrawing power of iminium. Therefore, pyrrole is less affected and thus has a smaller binding power than in the rear-substituted $(CH=C(CN))_n$ systems. (See the direction of the dipole moment in Figure 3a. In a three-component $(C(CN)=CH)_n$ system, pyrrole is to the left of this bridge and iminium is to the right. The
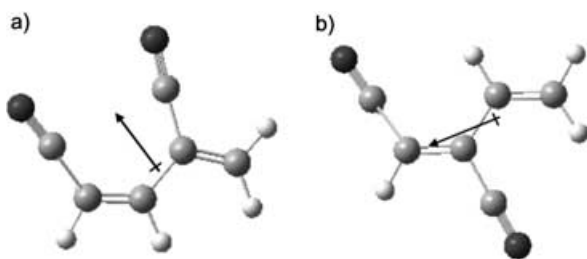

Figure 3. Directions of dipole moments of a) H−(C(CN)=CH−C(CN)=CH)−H (7.79 Debye) and b) H−(C(CN)=C(CN)−CH=CH)−H (1.56 Debye), calculated at the HF/6-31G(d) level.

dipole moment component along the ICT path has its negative end pointing to pyrrole and the positive end pointing to iminium. If the positive end is pointing to pyrrole, it is conceivable that it will be easier for pyrrole to donate its electrons.) The resisting power of the $(C(CN)=CH)_n$ bridges to protonation-induced ICT makes the $\Delta E_{b(P)}$ values decrease as quickly as the bridge length increases (Table 4).[21] Therefore, the three-component $(C(CN)=CH)_n$ systems are inferior to the rear-substituted $(CH=C(CN))_n$ systems. Compared to the unsubstituted bridges, the poorly positioned $(C(CN)=CH)_n$ bridges cause the $\Delta\Delta E_{b(P-N)}$ values to decrease by about 3.4 kcal mol^{-1} from $n = 1$ to 4, which is even larger than the decrease ($\approx$2.4 kcal mol^{-1})[6] for the corresponding pure vinyl bridges, $(CH=CH)_n$.

The dipole moment argument is also helpful in rationalizing the trend that $\Delta E_{b(P)}$ of $(C(CN)=C(CN)−CH=CH)_n$ are smaller than those of $(CH=CH−C(CN)=C(CN))_n$. (The direction of the dipole moment of H−(C(CN)=C(CN)−CH=CH)−H is shown in Figure 3b.) Another advantage of the $(CH=CH−C(CN)=C(CN))_n$ bridges over the $(C(CN)=C(CN)−CH=CH)_n$ is that their smaller $\Delta E_{b(N)}$ result in larger $\Delta\Delta E_{b(P-N)}$ and hence afford better signal transduction. It is easy to understand why the $\Delta E_{b(N)}$ of the $(CH=CH−C(CN)=C(CN))_n$ systems are smaller; without significant ICT in the neutral three-component systems, substituents closer to pyr-

role affect its binding ability more significantly. Electron-withdrawing substituents are far from the pyrrole moiety in the $(CH=CH−C(CN)=C(CN))_n$ systems, so binding the ability of pyrrole is lower than in the $(C(CN)=C(CN)−CH=CH)_n$ systems.

Although fluoro and cyano groups are both considered to be electron-withdrawing groups, the fluoro group also has a weak π-donating effect in addition to its σ-withdrawing property.[22] The weak electron-donating ability of the fluorine lone pair complicates the trends. For example, in a neutral three-component system, more electron-withdrawing substituents generally result in a larger $\Delta E_{b(N)}$ value. However, the trend of $\Delta E_{b(N)}$ of $(CH=CF)_n$ as n increases is different from all other neutral three-component systems; the longer the $(CH=CF)_n$ bridge, the weaker the pyrrole binding ability. We believe this is because F can donate its lone pair
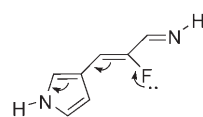
Scheme 3. Electron donation from the lone pair electrons of fluorine.

of electrons to pyrrole when it is substituted at the rear position (Scheme 3). When F atoms are substituted at the front positions, they can no longer donate electrons to the pyrrole moiety by means of π-conjugation so that only the σ-withdrawing effect is in operation. Therefore, $\Delta E_{b(N)}$ of $(CF=CH)_n$ increases as the bridge lengthens, as is expected for an electron-withdrawing substituent. Based on the dipole moment argument, the extent of ICT in protonated $(CH=CF)_n$ systems should be significantly better than in $(CF=CH)_n$. However, Table 4 shows that $\Delta E_{b(P)}$ of $(CH=CF)_n$ are only marginally better than those of $(CF=CH)_n$. This may also be related to the electron-donating power of F towards pyrrole at the rear position. Thanks to the decreasing $\Delta E_{b(N)}$ in longer bridges, the signal maintaining power of $(CH=CF)_n$ is virtually the same as that of $(CH=C(CN))_n$ (the range of $\Delta\Delta E_{b(P-N)}$ for both series is −6.9 to −5.1 kcal mol^{-1}) and better than that for fully substituted $(CF=CF)_n$. Although the conclusion that it is beneficial to place an electron-withdrawing group at the rear position (R^2) remains unchanged in spite of the complication of the fluoro electron-donating power, the combination of small $\Delta E_{b(N)}$/large $\Delta E_{b(P)}$ of the $(CH=CF)_n$ systems (compared to the pure vinyl bridges) provide a design strategy to create good signal transduction systems. When the front and rear positions are both substituted in a vinyl group, as in the $(CF=CF−CH=CH)_n$ and $(CH=CH−CF=CF)_n$ systems, the electron-donating power of a fluoro substituent becomes less obvious. The trends of binding energies and their differences can be understood with the same rationale mentioned for $(C(CN)=C(CN)−CH=CH)_n$ and $(CH=CH−C(CN)=C(CN))_n$ systems.

Given that rear positions (R^2) are better than front positions (R^1) in both $(CR^1=CR^2)_n$ and $(CR^1=CR^1−CR^2=CR^2)_n$ systems for a particular substituent, the next question naturally follows with respect to the design of a protonation-triggered signal-transducing conjugated system: is block substitution better than alternate substitution for systems with the

same bridge length (i.e., $(CH=CH-CR^2=CR^2)_m$ versus $(CH=CR^2)_{2m}$)? Figure 4 shows that the frontier orbitals of the bridges have an influence on ICT of protonated three-component systems. Examination of frontier orbitals of $H-(CH=CR^2)_{2m}-H$ and $H-(CH=CH-CR^2=CR^2_m-H$ molecules revealed that the substitution pattern has limited effects on HOMO energies (e.g., in Figure 4, HOMO energies of $H-$
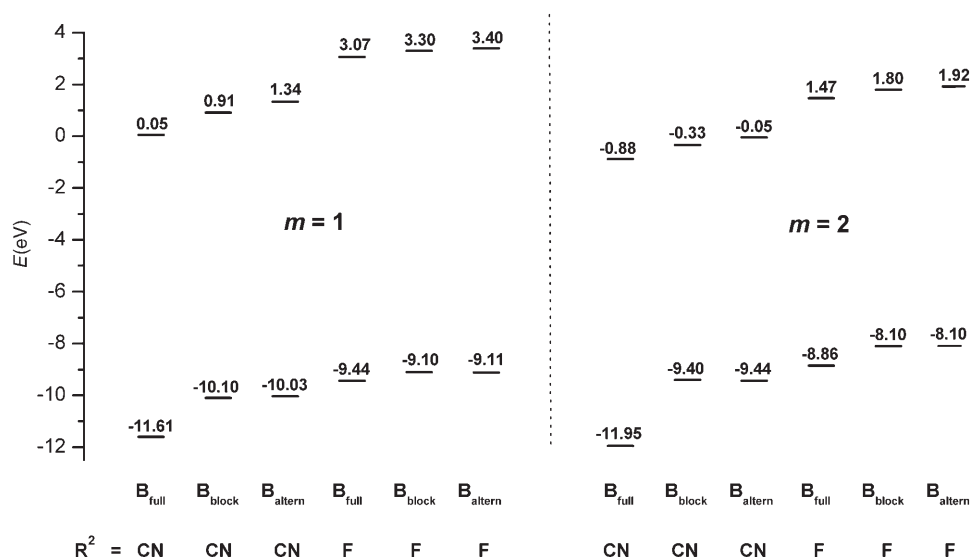
Although our aim was to control hydrogen bonds by protonation/deprotonation of D–B–A systems, the extents of ICT in a series of protonated D–B–A systems form an interesting research topic in its own right. To focus on the extents of ICT in different protonated π-conjugated systems, the relevant orbital energies of fully substituted $(CR=CR)_n$ bridges are also presented in Figure 4. If low HOMO and LUMO energies are preferred for ICT, as we suggested previously,[6b] the predicted order of ICT is $(C(CN)=C(CN))_{2m} > (CH=CH-C(CN)=C(CN))_m > (CH=C-(CN))_{2m} > (CF=CF)_{2m} > (CH=CH-CF=CF)_m > (CH=CF)_{2m}$. This order coincides with the trend of $\Delta E_{b(P)}$ for a given m. For example, for $m = 1$, the $\Delta E_{b(P)}$ values are -16.15, -14.66, -14.16, -13.31, -12.91, and -12.62 kcal mol^{-1}, respectively. In fact, protonation-induced polarization of a molecule is affected by many factors, not just the orbital energies of the bridge. However, the success of the current crude estimate indicates that, for closely related systems (e.g. all are vinyl-based and the bridge dipoles are not resisting ICT), there is room for a rational design based on simple chemical intuition.

Figure 4. π-HOMOs and π-LUMOs [eV] of 3 types of bridge substitution: full ($B_{full} = H-(CR=CR)_{2m}-H$), block ($B_{block} = H-(CH=CH-CR^2=CR^2)_m-H$) and alternate ($B_{altern} = H-(CH=CR^2)_{2m}-H$), where R and R^2 = CN or F and $m = 1$ or 2. The bridge with $m = 1$ (two C=C bonds) is shown on the left, the bridge with $m = 2$ (four C=C bonds) is shown on the right.

$CH=CH-C(CN)=C(CN)-H$ and $H-(CH=C(CN))_2-H$ are both approximately -10.1 eV and that of $H-(CH=CH-C(CN)=C(CN))_2-H$ and $H-(CH=C(CN))_4-H$ are approximately -9.4 eV). On the other hand, LUMO energies are more significantly affected by the substitution pattern; block substitutions always lead to lower LUMO energies than alternate substitutions. As the HOMO energies are similar, based on the trend of LUMO energies, one would expect that ICT should be more prominent in systems with block substitutions and therefore afford larger $\Delta E_{b(P)}$. This is indeed the trend observed for $\Delta E_{b(P)}$ (Table 4). The $\Delta E_{b(P)}$ of $(CH=CH-C(CN)=C(CN))_1$ and $(CH=C(CN))_2$ are -14.66 and -14.16 kcal mol^{-1}, respectively. Even with the complication of $\Delta E_{b(N)}$, the $\Delta\Delta E_{b(P-N)}$ results in Table 4 show that block substitution is superior to alternate substitution for a given bridge length, with the exception of the $\Delta\Delta E_{b(P-N)}$ values of $(CH=CH-CF=CF)_1$ and $(CH=CF)_2$, which are similar. However, from the viewpoint of signal maintenance, $(CH=CH-CF=CF)_m$ bridges should be preferred over $(CH=CF)_{2m}$ bridges. For $m = 1$ and 2, the $\Delta\Delta E_{b(P-N)}$ values of block substitution are -6.06 and -5.45 kcal mol^{-1}, respectively, whereas those of alternate substitution are -6.15 and -5.19 kcal mol^{-1}, respectively. Therefore, block substitution is superior for both the cyano and fluoro systems we examined.

It is curious that the π-HOMO orbitals of $H-(C(CN)=C(CN))_n-H$ do not increase as the conjugated system increases in length. We believe this is related to a significant nonplanarity of the bridge. The molecular structures and frontier orbitals of pyrrole–$(C(CN)=C(CN))_n$–imine and pyrrole–$(CF=CF)_n$–imine systems, $n = 1-4$, are shown in Figure 5. For neutral systems, structures of pyrrole–$(C(CN)=C(CN))_n$–imine show good planarity only when $n = 1$. Repulsion between the cyano groups has resulted in significant nonplanarity for systems with $n = 2-4$. A similar geometric distortion has also been observed in a recent theoretical study of decacyanooctatetraene.[23] When protonated, the geometry also shows planarity for $n = 1$ and nonplanarity for $n = 2-4$. Repulsion between fluoro groups is far less than between the cyano groups. Therefore, less severe nonplanarity is observed in the fluorinated systems (Figure 5b). The shapes of the molecular orbitals of the fluorinated systems are as expected; the HOMO and the LUMO are delocalized over the three-component systems. The electron-donating pyrrole contributes significantly to the HOMO and much less to the LUMO. The shapes of the frontier orbitals of the three-component cyano systems are very different (Figure 5a). Strong geometric distortion of the π-systems has caused localization of the orbitals. Moreover, while pyrrole
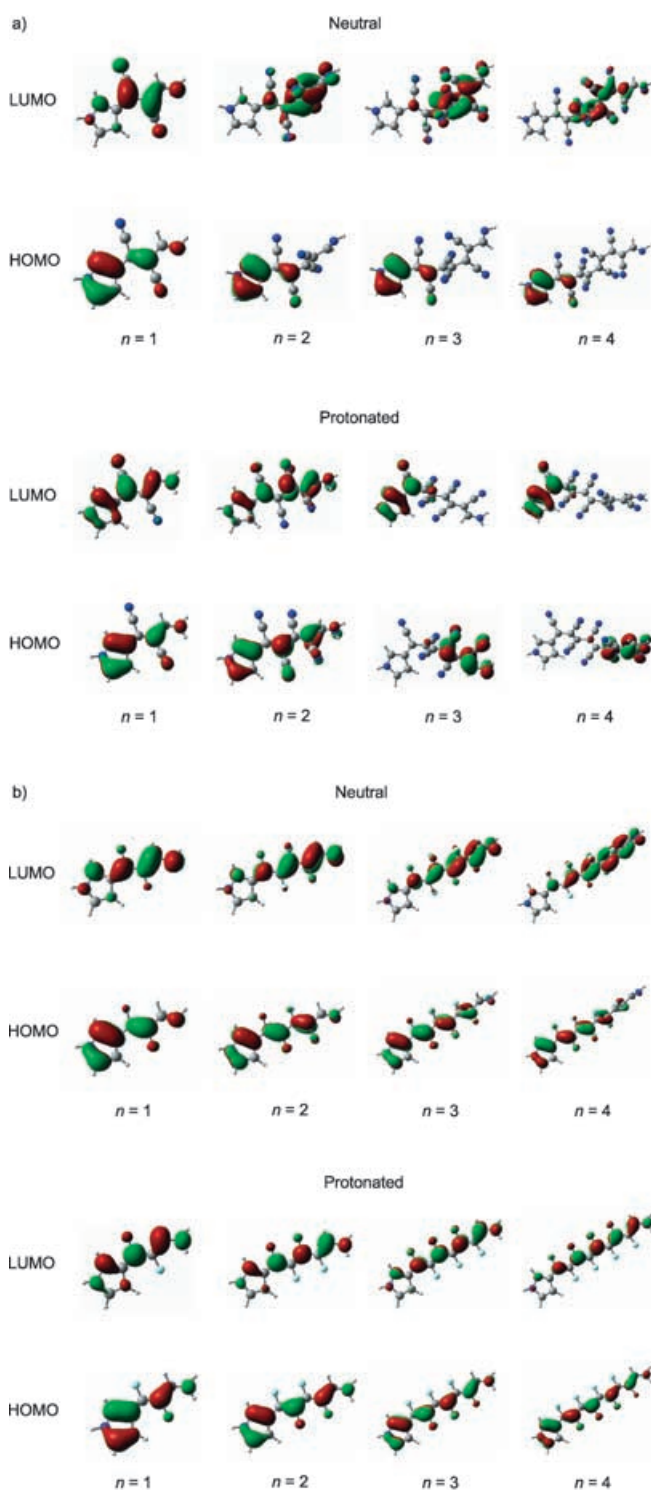
a)

Figure 5. a) MO diagram of pyrrole–(C(CN)=C(CN))$_n$–imine, n = 1–4.
b) MO diagram of pyrrole–(CF=CF)$_n$–imine, n = 1–4.

is facilitated by the strongly electron-withdrawing cyano bridges. This explains why pyrrole suddenly becomes a very strong hydrogen-bond donor in protonated cyano systems with n = 3–4 (Table 4). The similarity of frontier orbitals also explains why their $\Delta E_{b(P)}$ are similar (−20.00 and −20.40 kcal mol^{-1} for n = 3 and 4, respectively). Owing to the large $\Delta E_{b(P)}$, the $\Delta\Delta E_{b(P-N)}$ values are large as well. To confirm the HF/6-31G* results, calculations at the B3LYP/6-31G* were also carried out. At this level, nonplanarity is also observed for three-component systems with long cyano-bridges and the $\Delta E_{b(P)}$ value of (C(CN)=C(CN))$_4$ (−21.67 kcal mol^{-1}) is larger than that of (C(CN)=C(CN))$_2$ (−19.48 kcal mol^{-1}). The $\Delta\Delta E_{b(P-N)}$ values are −7.71 and −9.10 kcal mol^{-1} for n = 2 and 4, respectively, in agreement with the trend observed at the HF/6-31G* level. The important implication of these results is that one can design nonplanar systems to confine cation delocalization and thus achieve superb signal transduction and maintenance.

Conclusion

Protonation is used in this study to control the binding strength of designed D–B–A (pyrrole–bridge–imine) conjugated systems. The design strategy for the bridge (low bridge HOMO/LUMO) mentioned in a previous study[6b] was used to construct cyano and fluoro vinyl-based systems. When the substitution positions are properly chosen, the cyano group, which can result in a low bridge HOMO/LUMO, is a better substituent than the fluoro group with respect to facilitating the long-range protonation-induced ICT as proposed. In our previous studies, we found that the binding energies in the protonated state mainly determined whether the three-component systems were good signal transducers. Nevertheless, signal transduction is in fact determined by binding energies of both the protonated and the neutral states. The current study has broadened our perspectives by providing examples in which the binding energy in the neutral state is an important factor. The (CH=CF)$_n$ systems demonstrate that the electron-donating power of lone pairs of a fluoro group are useful in generating a small $\Delta E_{b(N)}$ at the pyrrole end. The (CH=CH−CR=CR)$_n$ block substitution systems demonstrate that placing electron-withdrawing substituents away from the pyrrole binding center can result in small $\Delta E_{b(N)}$ and large $\Delta E_{b(P)}$.

Overall, three important insights are provided in this study. First, substitution positions/patterns are important; with well-planned positions, substituents of weak electronic effects can still be useful in constructing effective three-component systems. Second, the idea of achieving good signal transduction by maximizing the extent of ICT has evolved into creating a system with a small $\Delta E_{b(N)}$ and/or a large $\Delta E_{b(P)}$. Finally, with proper constituents of the three-component system, nonplanarity of the bridge could be used to facilitate charge localization and help to maximize the extent of ICT. Our study not only contributes to the rational realization of remote control of binding, but also provides a fun-

contributes to the HOMO of the neutral three-component systems and to the short protonated systems (n = 1–2) as expected, it contributes significantly to the LUMO of the protonated systems with n = 3–4 and totally disappears in their HOMO, indicating strong ICT from pyrrole to iminium

damental understanding of the neutral/protonated D–B–A conjugated systems.

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