Through-Space Exciton Coupling and Multimodal Na$^+$/K$^+$ Sensing Properties of Calix[4]arenecrowns with the Thienylene Analogue of *para*-Terphenoquinone as Chromophore**

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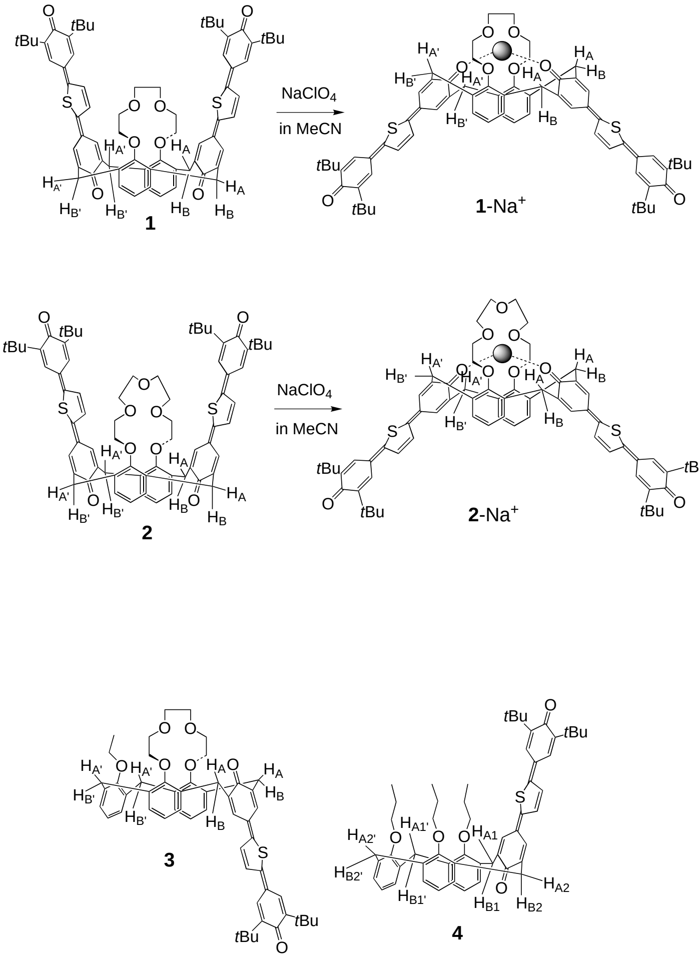
Calix[4]arenes are today utilized as excellent platforms or shaping units for creating attractive host molecules with ion-sensing properties.[1] In the nineties, chromogenic recognition by chromophore-derived calix[4]arenes[2] and electrochemical recognition by quinone-derived calix[4]arenes[3] of alkali metal cations were reported. However, as far as we know, there are no reports on through-space interactions between two chromophores incorporated in a calixarene skeleton, although a paper dealing with intramolecular electron transfer in calix[4]arenediquinone derivatives appeared quite recently,[4] and multifunctional ion-sensing calixarenes that combine chromogenic and redox-active properties in one molecule are unknown. The combination of these properties could offer a promising route towards novel sensing materials.

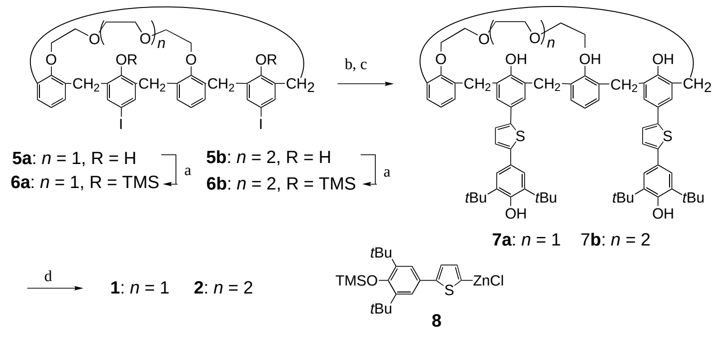
We have now designed and synthesized the novel calix[4]arenecrowns **1** and **2**, together with their reference compounds **3** and **4**, since the thienylene analogue of *p*-terphenoquinone as chromophore shows a strong absorption maximum in the visible region and affords a very stable radical anion and radical cation in electrochemical reactions.[5] We found that the two diametrically arranged chromophores of **1** and **2** undergo through-space exciton coupling on absorption of visible light. The transition dipole moment in the exciton coupling[6] is strongly influenced by a conformational change of the two interacting chromophores. A remarkable conformational change indeed occurred in **1** and **2** upon complexation of Na$^+$ or K$^+$ ions (Scheme 1), which resulted in a significant color change. Moreover, **1** and **2** can also recognize electrochemically Na$^+$ and K$^+$ ions.[7] Thus, **1** and **2** are the first ion-sensing host molecules that exhibit both chromogenic and electrochemical recognition properties.



Scheme 1. The calix[4]arenecrowns **1** and **2** and the reference compounds **3** and **4**. Formation of **1**-Na$^+$ and **2**-Na$^+$.

The synthesis of **1** and **2** (Scheme 2) started from the diiodo compounds **5a**[8] and **5b**,[8] respectively. The reference monoheteroquinones **3** and **4** were synthesized by similar routes.[9]

Compound **4** adopts a partial cone conformation both in the solid state and in solution, which was confirmed by X-ray crystal structure analysis[10] and by the ^{1}H NMR spectrum,[9]



Scheme 2. Synthesis of the calix[4]arenecrowns **1** and **2**. a) BSA, MeCN, CHCl$_3$, reflux, **5a**: 50%, **5b**: 50%; b) **8**, cat. Pd^0, THF, 25°C; c) TBAF, THF, 25°C, **7a**: 31%, **7b**: 28%; d) PbO$_2$, CH$_2$Cl$_2$, 25°C, **1**: 92%, **2**: quantitative. BSA = *N*,*O*-bis(trimethylsilyl)acetamide, TMS = trimethylsilyl, TBAF = tetrabutylammonium fluoride.

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which gave the differences in calix methylene proton chemical shifts: $\Delta\delta(H_{B1},H_{A1}) = 0.33-0.26$, $\Delta\delta(H_{B2},H_{A2}) = 0.38-0.31$, and $\Delta\delta(H_{B1'},H_{A1'}) \approx \Delta\delta(H_{B2'},H_{A2'}) = 1.00-0.98$. Compound **3** adopts a cone conformation in solution, since the chemical shift differences $\Delta\delta(H_B,H_A) = 1.54-1.48$ and $\Delta\delta(H_{B'},H_{A'}) = 1.22-1.21$ are large. In contrast, **1** exists in a 1,3-alternate conformation in solution, since the chemical shift differences $\Delta\delta(H_B,H_A) \approx \Delta\delta(H_{B'},H_{A'}) = 0.29-0.18$ are very small. Compound **2** also exists in a 1,3-alternate conformation, as inferred from the small $\Delta\delta(H_B,H_A)$ and $\Delta\delta(H_{B'},H_{A'})$ values of 0.64–0.45.[11]

Compounds **1**–**3** form 1:1 complexes with Na^+ ions under saturation conditions. The most stable conformation of **1**-Na^+ is a cone structure, since the $\Delta\delta(H_B,H_A) \approx \Delta\delta(H_{B'},H_{A'}) = 1.07-1.03$ values are large. The complex **2**-Na^+ also exists in a cone conformation, as inferred from the ^1H NMR spectrum ($\Delta\delta(H_B,H_A) \approx \Delta\delta(H_{B'},H_{A'}) = 1.13-1.10$). Hence, **1** and **2** have the 1,3-alternate conformation and undergo ring inversion to the cone conformations upon complexation. Interestingly, the bulky thienylene analogues of *p*-terphenoquinone rotate from above to below the calixarene macrocyclic plane.

The structures of **1** and **1**-Na^+ were optimized by molecular orbital (MO) and molecular mechanics (MM) methods. Optimization at the HF/3-21G level (Gaussian 94[12]) was first performed for the free form and then for the Na^+ complex of 1,3-bis(*p*-benzoquinonemethide)-derived calix[4]-arenecrown-4. Then, by retaining the MO-optimized structure and replacing the methide groups by 2-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene-5-ylidene groups, the MM optimization was executed.[13] The resulting 1,3-alternate conformation of **1** and the highly flattened cone conformation of **1**-Na^+ are shown in Figure 1. In the optimized cone **1**-Na^+, the Na^+ ion lies at the center of the crown ether bridge, 2.3 Å from the four crown oxygen atoms and 2.2 Å from the quinone oxygen atoms.

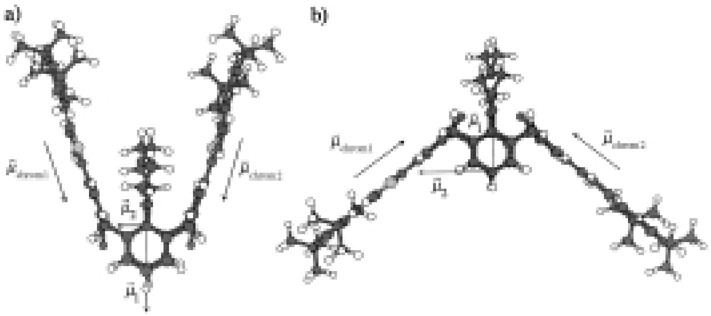

Figure 1. Side views of the molecular structures of a) **1** and b) **1**-Na^+, indicating the transition dipole moments.

Whereas the monoheteroquinone **3** exhibits only one intense absorption band at 568 nm in the electronic spectrum (Figure 2a), the bis-heteroquinone **1** exhibits two absorption bands in the visible region at 540 and 579 nm, of which the band at shorter wavelength has a higher intensity than that at longer wavelength (Figure 2b).[9] Upon addition of $NaClO_4$ to an acetonitrile solution of **1**, the intensity of the longer wavelength band increased, and that of the shorter one decreased, accompanied by the appearance of a new broad and weak band at around 630 nm (Figure 2b). In consequence, the color of the solution turned from purple to blue. This spectroscopic feature is excellently reproduced by INDO/s calculations[14] on **1** and **1**-Na^+ based on the MO-MM optimized structures when through-space exciton coupling between the two diametrically arranged chromophores is taken into account. As shown in Table 1, there is a fairly good agreement between experimental and theoretical values of $\lambda1_{max}$ and $\lambda2_{max}$, as well as for the reversal of the absorption intensity upon complexation.[15] In exciton coupling systems,[6] the excited state splits into two energy levels due to the interaction between the two transition dipole moments (out-of-phase (α state) and in-phase (β state) combinations of the transition dipole moment vectors), which is indicated by a splitting of the absorption band. According to the INDO/s results the splitting of the absorption band does indeed result from the combination of the two individual transition dipole moments μ_{chrom1} and μ_{chrom2}, that is, exciton coupling takes place. The two individual dipole moments almost lie in the molecular planes of the two chromophores. Hence, the angle between the two chromophores determines the relative intensity of the two absorption bands. The angle between μ_{chrom1} and μ_{chrom2} for the Na^+-free form of **1** in the 1,3-alternate conformation is estimated to be about 43°. According to the exciton coupling theory, if the angle is less than 90°, as in this case, the α state combination becomes energetically more stable than the β state combination. The transition to the β state at shorter wavelengths gives rise to a more intense

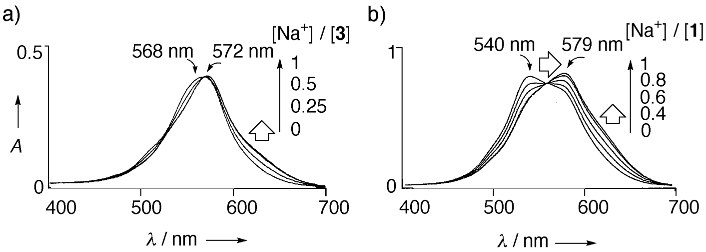

Figure 2. Spectroscopic changes upon addition of $NaClO_4$ to a solution of a) **3** and b) **1** in MeCN. A = absorbance.

Table 1. Observed and calculated[a] electronic spectral data of the calix[4]arenequinones **1** and **3**, and their Na^+ complexes.

Compound	Calculated				Observed (in MeCN)			
	$\lambda1_{max}$ [nm]	f	$\lambda2_{max}$ [nm]	f	$\lambda1_{max}$ [nm]	ε	$\lambda2_{max}$ [nm]	ε
1	555	0.68	493	4.78	579	105758	540	118856
1-Na^+	575	3.12	515	1.99	579	124546	540	97396
	λ_{max} [nm]	f			λ_{max} [nm]	ε		
3	529	2.56			568	81127		
3-Na^+	549	2.54			572	83129		

[a] INDO/s calculation.

band than that to the α state at longer wavelengths, because the intensity is proportional to the square of the sum of the vectors. In contrast, the angle between μ_{chrom1} and μ_{chrom2} is estimated to be about 106° for the cone **1**-Na$^+$, that is larger than 90°. In this case, the β state becomes more stable than the α state, and the longer wavelength band has the higher intensity. This explains the reversal of the intensity of the two maxima on going from **1** to **1**-Na$^+$ (Figure 2b).

The crown-5 bridged bis-heteroquinone **2** also exhibits two absorption maxima (at 542 and 577 nm; Figure 3). Although the reversal of the intensities on going from **2** to **2**-Na$^+$ is not so pronounced as in the case of **1**, the occurrence of exciton coupling is strongly supported by the electronic spectral feature shown in Figure 3.

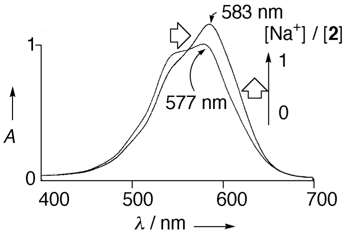

Figure 3. Spectroscopic changes upon addition of NaClO$_4$ to a solution of **2** in MeCN. A = absorbance.

The INDO/s calculations on the monoquinones **3** and **3**-Na$^+$[16] gave only one absorption maximum and reproduced well the experimental values (Table 1). The observation of exciton coupling for **1** and **2** reveals that the conformational fixation in these compounds appears to be fairly good even in solution. This is the first observation of through-space dipole interactions between two chromophores in calixarene systems.

Significant changes in the spectra of **1** and **3** were not observed even after 18 equivalents of KPF$_6$ were added. However, a spectral change similar to that shown in Figure 3 was clearly observed on addition of one equivalent of KPF$_6$ to **2**. Indeed, crown-4-bridged **1** and **3** showed 100- to 1000-fold higher selectivity for Na$^+$ versus K$^+$ than crown-5-bridged **2** with its larger ionophoric cavity (Table 2).

As shown in Table 3, the first half-wave reduction potential E_{red}^{1} of **1**, **3**, and **2** shifted anodically (stabilization shift) by $\Delta E = 250$, 250, and 170 mV, respectively, on addition of NaPF$_6$. Interestingly, a similar anodic shift of $\Delta E = 200$ mV was also observed for **4**, although the association constant for the complexation of the non-crown-bridged **4** with Na$^+$ is more than 10^4 times smaller than that of the crown-4-bridged **3**. These facts indicate that a significant Na$^+$ binding enhancement occurs when the chromophores are reduced to the corresponding radical anions, that is, the complexes with the alkali metal ions are thermodynamically much more stable in the radical anion state than in the neutral state of the heteroquinone moieties. Thus, **4** can act as a redox-switching Na$^+$ transporting mediator due to the significant difference in the binding capability between the neutral state and the radical anion. In terms of the ΔE values of the reduction potentials, the electrochemical Na$^+$/K$^+$ selectivity of **1** is still higher than that of **2**.

Table 2. Association constants K[a] for the 1:1 complexes of **1**–**3** with Na$^+$ and K$^+$, determined by UV/Vis titration in MeCN at room temperature.

Compound	K(Na$^+$)	K(K$^+$)
3	$> 1.2 \times 10^6$	7.0×10^2
1	$> 1.2 \times 10^6$	4.7×10^3
2	$> 1.2 \times 10^6$	$> 1.2 \times 10^6$

[a] Obtained by processing UV/Vis data using a nonlinear least square curve fitting computer program.

Table 3. Redox potentials E in V[a] of the calix[4]arenes **1**–**4**, and the anodic shifts ΔE in mV in the presence of five equivalents of NaPF$_6$ or KPF$_6$ in PhCN.

Compound		E_1^{red}	E_2^{red}	$E_{\text{p1}}^{\text{ox}}$
4	E(free)	−0.51	−0.76	+1.23
4	ΔE(Na$^+$)[b]	200	240	10
3	E(free)	−0.50	−0.70	+1.21
3	ΔE(Na$^+$)[b]	250	170	160
1	E(free)	−0.52	−0.68	+1.21
1	ΔE(Na$^+$)[b]	250	170	160
1	ΔE(K$^+$)[c]	150	100	130
2	E(free)	−0.51	−0.68	+1.30
2	ΔE(Na$^+$)[b]	170	100	30
2	ΔE(K$^+$)[c]	140	90	20

[a] 0.1 M TBAP, vs. SCE, scan rate 50 mV s^{-1}. E_1^{red} and E_2^{red} are the first and second half-wave reduction potentials, respectively. $E_{\text{p1}}^{\text{ox}}$ is the first oxidation peak potential. [b] In the presence of five equivalents of NaPF$_6$. [c] In the presence of five equivalents of KPF$_6$ in PhCN:MeCN = 5:1 v/v.

If there is an unfavorable interaction between an encapsulated positively charged Na$^+$ or K$^+$ ion and the heteroquinone moieties in radical cation form, the alkali metal ion binding is anticipated to become much more difficult when the heteroquinone chromophores are oxidized. However, as shown in Table 3, large anodic shifts (destabilization shifts) of the oxidation potentials $E_{\text{ox}}^{\text{p1}}$ by $\Delta E = 160$ mV are observed for **3** and **1** on binding an Na$^+$ ion, and this indicates that the binding capabilities of the crown-4 bridges of **3** and **1** for Na$^+$ ions are so strong that the unfavorable interaction can easily be overcome. The relatively small anodic shifts in $E_{\text{ox}}^{\text{p1}}$ of **2** can be ascribed to a weak destabilizing interaction owing to the loose contact between the encapsulated Na$^+$ or K$^+$ and the carbonyl oxygen atoms of the radical cation of the heteroquinone moieties of **2.** Thus crown-4-bridged **1** is an especially novel host molecule that senses Na$^+$/K$^+$ by the induction of pronounced electrochemical anodic shifts not only in the reduction potential but also in the oxidation potential.

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[9] Compounds **1**–**4** were synthesized as 1:1 mixtures of isomers having different orientations of the sulfur atom of the thienylene analogue(s) of *p*-terphenoquinone, since four different *t*Bu signals and four different signals for the quinoid ring protons α to CH_2 for **1** and four different thienyl ring proton signals for **2** were observed in the ^{1}H NMR spectra (600 MHz, $CDCl_3$, 25°C, TMS). All spectral data were recorded on the mixtures. **1**: m.p. 128–129°C; ^{1}H NMR: δ = 1.340, 1.342, 1.36, 1.37 (four singlets, 9H each, *t*Bu), four pairs of doublets at 3.58, 3.59, 3.61, 3.63 (H_A, $H_{A'}$) and at 3.81, 3.84, 3.84, 3.87 (H_B, $H_{B'}$, ^2J(H,H) = 14 Hz); IR (KBr): $\tilde{\nu}$ = 1590 cm^{-1} (C=O); UV/Vis (MeCN): λ_{max} (lgε) = 579 (5.02), 540 (5.08), 496 sh (4.59), 349 (4.24), 332 (4.09), 284 (4.18), 273 (4.20), 262 (4.18); FAB-MS: *m*/*z* (%): 1129 (100) [M^++Na^+], 1108 (61) [M^++2], 1106 (23) [M^+]. **2**: m.p. 223–225°C; ^{1}H NMR: δ = 1.37, 1.38, (two singlets, 18H each, *t*Bu), 3.36 and 3.40 (H_A, $H_{A'}$, ^2J(H,H) = 14 Hz), 3.85–4.00 (H_B, $H_{B'}$); IR (KBr): $\tilde{\nu}$ = 1593 cm^{-1} (C=O); UV/Vis (MeCN): λ_{max} (lgε) = 577 (5.06), 542 (5.05), 499 sh (4.63), 350 (4.26), 336 sh (4.19), 298 (4.06), 283 (4.09), 274 (4.11); FAB-MS: *m*/*z* (%): 1154 (100) [M^++4], 1153 (54) [M^++3], 1150 (5) [M^+]. **3**: m.p. 240–241°C; ^{1}H NMR: δ = 1.32, (s, 9H, *t*Bu), 1.37, (s, 9H, *t*Bu), two pairs of doublets at 2.93 or 2.96 (H_A) and 4.44 or 4.47 (H_B) (^2J(H,H) = 16 Hz), two pairs of doublets at 3.24 and 3.24 ($H_{A'}$) and 4.45 or 4.46 ($H_{B'}$) (^2J(H,H) = 14 Hz); IR (KBr): $\tilde{\nu}$ = 1589 cm^{-1} (C=O); UV/Vis (MeCN): λ_{max} (lgε) = 568 (4.91), 488 sh (4.07), 347 (3.97), 334 sh (3.89), 281 sh (3.83), 273 (3.86), 263 (3.84); FAB-MS: *m*/*z* (%): 873 (39) [M^++Na^+], 852 (100) [M^++2], 850 (8) [M^+]. **4**: m.p. 252–253°C; ^{1}H NMR: δ = 1.37 (s, 9H, *t*Bu), 1.39 (s, 9H, *t*Bu), four pairs of doublets of the methylene protons at 3.48 (H_{A1}), 3.43 (H_{A2}) (^2J(H,H) = 12 Hz), 3.74–3.81 (H_{B1}, H_{B2}, $CH_3CH_2CH_2$), 3.09 and 3.10 ($H_{A1'}$, $H_{A2'}$), 4.08 or 4.09 ($H_{B1'}$, $H_{B2'}$) (^2J(H,H) = 13 Hz); IR (KBr): $\tilde{\nu}$ = 1591 cm^{-1} (C=O); UV/Vis (MeCN): λ_{max} (lgε) = 566 (4.74), 509 sh (4.28), 350 (3.73), 334 (3.65), 294 (3.66), 277 (3.77), 272 (3.78); FAB-MS: *m*/*z* (%): 836 (100) [M^++2], 834 (7) [M^+].

[10] Single crystals of **4**: monoclinic, space group $P2_1/n$, $Z = 4$, $a = 15.684(4)$, $b = 10.589(4)$, $c = 29.278(4)$ Å, $\beta = 96.52(2)°$, $V = 4830(2)$ Å^3 ($R = 0.114$ and $Rw = 0.140$ for 2393 observed reflections with $I > 3.00\sigma(I)$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137583. 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).

[11] Compounds **1**–**4** do not exist as mixtures of different conformers. This was proved by NMR spectroscopic analyses with DEPT, HMQC, HMBC, ^{1}H-^{1}H COSY, and ^{13}C-^{1}H COSY methods.

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[13] The MM calculations were performed with the Cerius 2 graphics package by using the universal force field (UFF).

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[15] In addition to the calculated absorption bands listed in Table 1, a new, forbidden transition, assignable to the weak absorption band at around 630 nm (Figure 2), resulted for **1**-Na^+ and **3**-Na^+ only when the Na^+ ion was taken into account in the INDO/s calculation. Therefore, this weak band may originate from the ion–dipole interaction between the encapsulated alkali metal cation and the carbonyl groups of the heteroquinones.

[16] Stable cone conformations were optimized for both **3** and **3**-Na^+ with the same calculation method as for **1** and **1**-Na^+.

In Situ ^{1}H MAS NMR Spectroscopic Observation of Proton Species on a Mo-Modified HZSM-5 Zeolite Catalyst for the Dehydroaromatization of Methane[**]

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Zeolites and oxide-modified zeolites have been widely used in light-paraffin aromatization reactions.[1, 2] It has been generally accepted that the acidic sites, together with the dehydrogenation centers of the metal oxide components, play key roles in paraffin activation and the subsequent aromatization. In 1993, we were the first to report that methane, an ultra stable molecular, could undergo aromatization on molybdenum modified HZSM-5 catalysts under nonoxidative conditions.[3] Subsequent investigations[4] demonstrated that the Brønsted acidity and the channel structure of the zeolites, as well as the oxidation states of the Mo species, are crucial factors that affect the performance of the catalysts. However, most of the discussions concerning the nature of the active species, for instance the location of the Mo species on or in the zeolite and the variation of the zeolitic acidity, are based on data obtained from off-line characterizations using "ideal" catalysts under conditions far from those in the real catalytic processes.[4a–e]

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