ACES Asian Chemical Editorial Society

DOI: 10.1002/asia.201901424

CHEMISTRY AN ASIAN JOURNAL Communicatio

Check for updates

A Hydrosilylation Approach to Silicon-Bridged Functional Dipyrromethanes: Introducing Silicon to A New Arena

Bhaskar Garg,*[a] Tanuja Bisht,[b] and Yong-Chien Ling[c]

Dedicated to Prof. S. M. S. Chauhan

Abstract: Two silylene-spaced ((*E*)-vinylsilyl)anthracene-dipyrromethane dyads have been designed and synthesized by $RhCl(PPh_3)_3$-catalyzed hydrosilylation reactions of 5-methyl-5′-(ethynylaryl)dipyrromethanes with (9-Anthryl)-dimethylsilane. The complexation studies of dyads toward different anions have also been performed, which reveal that dyads exhibit a highly selective response towards fluoride anion attributable to both hydrogen-bonding and pentacoordination phenomena. This dual-mode fluoride recognition event is unprecedented and may pave the way for future developments in the areas of porphyrinoids, organosilicon, polymer, and supramolecular chemistry.

Since the pioneer synthesis of first compound, tetraethyl silane, unarguably, the organosilicon chemistry has come a long way with all ups and downs, and currently, making a profound impact on both industrial and academic settings at the interface of synthetic organic chemistry, polymer chemistry, medicinal chemistry, materials science, and in the development of fluorescent sensors with improved biological attributes.[1,2] Fascinating this "aura" of organosilicon compounds and appreciable as this scientific progress are, studies pertaining synthetic pyrrolic systems within silicon domain are still very limited. Consequently, there remains an urgent need to develop new organosilicon compounds so that the ability of silicon to bridge the gap between different disciplines could be truly realized. In this context, the pyrrolic receptors such as dipyrromethanes (DPMs) are particularly appealing.

DPMs are of utmost importance in organic synthesis, namely, porphyrinogens and related macrocycles. Owing to the presence of two pyrrolic NHs as hydrogen bond donor sites, DPMs have emerged as versatile anion receptors either on their own or as building blocks within more complex settings such as calix[4]pyrroles (CPs).[3] Highly efficient organic reactions or diverse strategies have been extensively applied for many years as a powerful tool for structure modifications, and modulation of anion-binding properties of DPMs and CPs.[3–5] Undoubtedly, these intellectual efforts have transformed one's ability to better understand the chemistry of these pyrrolic systems as well as the concepts in supramolecular chemistry. Nevertheless, within this "tool box" of chemical functionalization of DPMs or CPs, an efficient reaction which has never received any attention as we think it merits is catalytic hydrosilylation reaction.[6] This scientific apathy has left the literature limited to only some elegant silicon complexes of DPMs and CP bearing N–Si bond.[7]

We initially envisioned that *meso*-substituted "two-wall" aryl extended CP with alkyne groups at aromatic walls[8] might serve as an embryonic system to incorporate silylene spacer between CP and an appropriate signaling motif, following hydrosilylation reaction. At this juncture, however, it would be worthwhile to emphasize that controlling the regiochemistry of alkyne hydrosilylation is especially challenging due to the formation of several isomers (Upper Panel, Scheme 1).[6b] Aside from that, the formation of stereoisomers of aryl-extended CPs in significantly low yields is another penalty essentially encountered in their synthesis.[5d,8,9] With such considerations in mind, 5,5′-alkylaryl DPMs, "better half" of aryl-extended CPs appeared quite attractive to us in order to develop a new class of silicon-containing synthetic pyrrolic receptors as well as to investigate the role of silicon atom on the anion-induced coordination events.

Herein, we report the synthesis, characterization, and anion-complexation properties of two novel Si-bridged anthracene-DPM dyads, **5a** and **5b**, that are to the best of our knowledge without precedent in the literature.

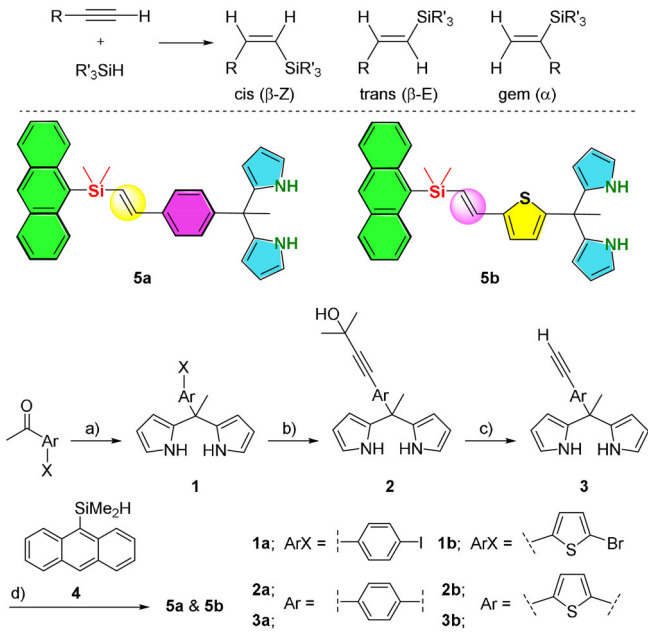
The structures and synthesis of target compounds **5** are outlined in Scheme 1. *Meso*-substituted DPMs **1** were prepared by minor modifications of known procedures.[8,10] **1**, in turn, could be carried on to the key-protected alkynyl derivatives **2** by exposure to an excess of alkynyl alcohol in TEA-toluene at 60 °C in the presence of $Pd(PPh_3)_2Cl_2$-CuI.[11] The deprotection of **2** with NaOH afforded moderately sensitive alkyne precursors **3a** and **3b** in 72% and 64% yields, respectively. **3a** and **3b** were kept at low temperature prior to use further. The synthesis of (*9-Anthryl*)-dimethylsilane precursor **4** was accomplished in two steps. Specifically, the lithiation of 9-bromoanthracene with *n*-BuLi at −78 °C followed by treatment with Me_2SiHCl in THF af-

[a] *Dr. B. Garg*
Department of Chemistry
Indian Institute of Technology Roorkee
Roorkee 247667, Uttarakhand (India)
E-mail: bhaskargarg111@gmail.com

[b] *Dr. T. Bisht*
Department of Chemistry
Government Girls P. G. College
Haldwani 263139 (India)

[c] *Prof. Dr. Y.-C. Ling*
Department of Chemistry
National Tsing Hua University
101, Section 2, Kuang-Fu Road, Hsinchu 30013 (Taiwan) (ROC)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/asia.201901424.



Scheme 1. Upper panel: A schematic for hydrosilylation reaction of alkynes with possible stereoisomers. Lower panel: Synthesis of silylene-spaced functional dipyrromethane dyads **5**. Reagents: a) pyrrole, CF_3CO_2H; b) $Pd(PPh_3)_2Cl_2$, CuI, 2-methyl-3-butyn-2-ol; c) NaOH; and d) Wilkinson's catalyst.

forded **4** as shiny yellow crystals in 59% yield after chromatographic work up, and subsequent recrystallization with EtOH. Once both precursors in hand, the hydrosilylation reaction between **3a** and **4** was screened and optimized under a variety of conditions.[12] As such, the slow addition of **4** into a solution of **3a** in toluene (0.2 M) in the presence of Wilkinson's catalyst and KI gave **5a** as dark brown solid in 12% yield after column chromatography (silica gel; DCM-hexane: 8:2, v/v). However, **5b** could be isolated in quite low yield (ca. 2.9%) under virtually identical reaction conditions. The isolation of **5** in low yields against the reputation of standard hydrosilylation reaction, in general, can be attributed to scrambling together with the sensitivities of **3a** and **3b**, which possibly decompose during the course of hydrosilylation reactions, resulting in the recovery of **4** in ca. 15–23% yields. The structures of all intermediates and bench stable dyads **5** were characterized by different spectroscopic techniques (Figures S1–S27 in the Supporting Information).

The ^{1}H NMR spectrum of **5a** recorded in $CDCl_3$ (Figure 1) displayed a single NH resonance at δ 8.51 ppm, which was slightly downfield shifted as compared to the DPMs **1a**–**3a**. The four distinctive resonances at δ 8.53 (1H), 8.03 (2H), 7.81 (2H), and 7.44 (4H) ppm could be assigned to anthryl protons with ease. In addition, two sharp singlet resonances at δ 2.04 and 0.83 ppm were corresponded to the *meso*- and silylene-methyl protons, respectively (Figure S18 in the Supporting Information). Most importantly, an unequivocal proof about the stereochemistry that is, *trans*-configuration of **5a** was accessed by the characteristic signals at δ 6.93 (H_a) and 7.03 (H_b) ppm (as highlighted in yellow background, in Figure 1a), which furnished large coupling constants ($J = \sim 19$ Hz) for the vinyl group. The absence of any resonance around δ 6.5 ppm ($J \approx 15$ Hz) ruled out the possibility of any *cis*-vinylene bonds. The ^{1}H NMR resonating pattern of **5a** for rest of the signals (aryl and pyrrolic) were found nearly the same relative to those of **1a**–**3a**.

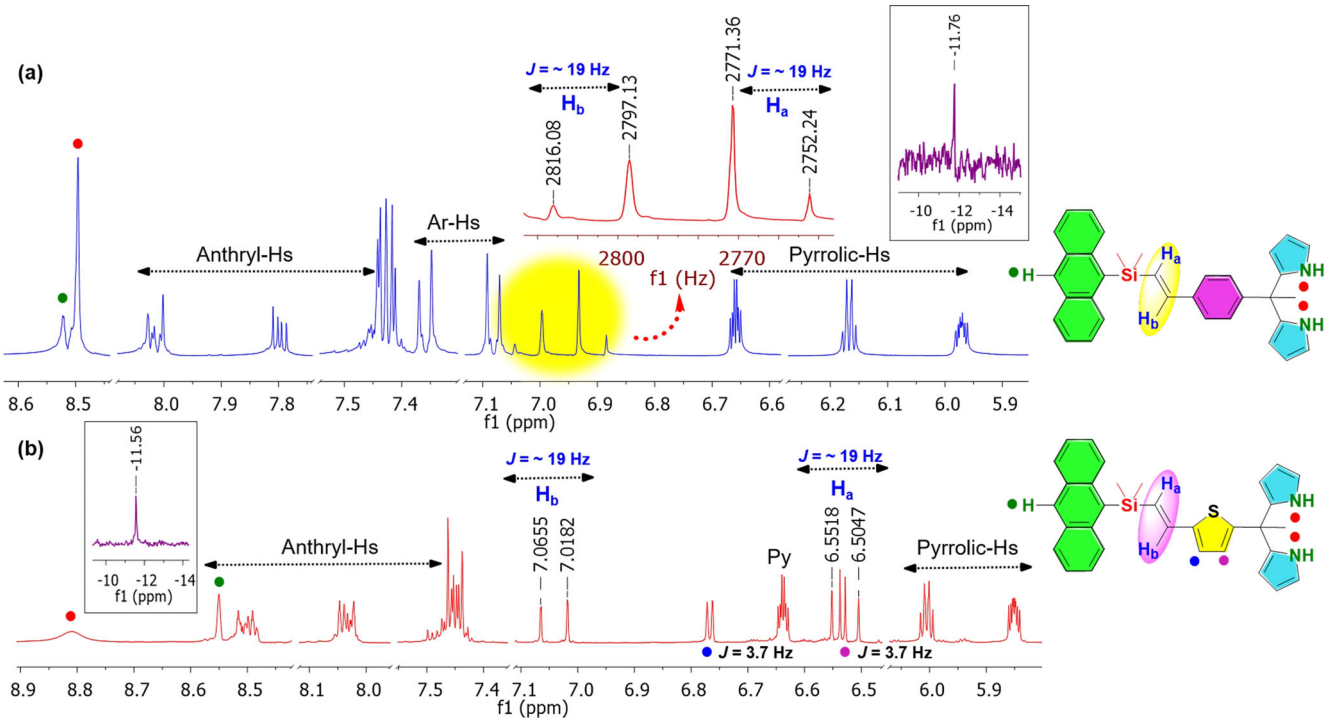


Figure 1. Selected regions of the ^{1}H NMR (400 MHz) spectra of (a) **5a** and (b) **5b** acquired in $CDCl_3$ and $[D_3]CH_3CN$, respectively, at 298 K. Inset (in violet): the corresponding ^{29}Si{^{1}H} NMR (80 MHz) spectra of **5a** and **5b**. The molecular structures with colored dots and circles indicate specific proton assignments.

In contrast to **5a**, the overlapping and significant broadening of most proton signals of **5b** hampered its characterization in $CDCl_3$. However, all proton signals were well resolved in $[D_3]CH_3CN$ and could be assigned with ease as shown in Figures 1b and S19.

The ^{1}H NMR structural assignments of **5a** and **5b** were found in agreement with those of ^{13}C and ^{29}Si NMR spectra of **5a** and **5b** (Figures S20-S23 in the Supporting Information). Specifically, the ^{29}Si{^{1}H} NMR spectra of **5a** and **5b** in $CDCl_3$ exhibited a single resonance at δ −11.76 and −11.56 ppm, respectively (Insets, Figure 1), which registered a significant downfield shift relative to that of silane precursor **4** (δ = −25.98 ppm).

^{1}H NMR titrations were performed to probe the complexation behavior of **5a** towards different anions (F^-, Cl^-, AcO^-, $H_2PO_4^-$ and CN^-) as their tetrabutylammonium (TBA) salts. Typically, aliquots of the putative anionic guests (0.2 M) were added to a solution of **5a** (0.02 M) in $[D_6]$DMSO, and the shift of the NHs along with other protons recognized after each addition.

As shown in Figure 2A, upon gradual addition of F^-, the pyrrolic NHs originally appearing at δ 10.3 ppm constantly shifted downfield and finally split by interaction with ^{19}F nucleus ($\Delta\delta \approx 4.25$ ppm; $J_{HF} = 23.5$ Hz), a hallmark of strong binding.[13] Furthermore, the absence of any resonance around δ 16 ppm ($J \approx 117$ Hz) completely ruled out the possibility of any deprotonation.[14,5c] Besides NHs, interestingly, a noticeable downfield shift for one set of β-pyrrolic protons (H_4; $\Delta\delta$ = 0.21 ppm) was also observed, and that could be attributed to the ring current effect of the phenyl group associated with increasing rigidity of the molecule upon F^- complexation (Figure S28 in the Supporting Information). Nevertheless, a "through-bond" propagation effect was evident for protons H_2, H_3, H_5 and H_6, which all experienced a shielding effect; significantly higher for H_5 and H_6 ($\Delta\delta$ = 0.18–0.32 ppm) than those of H_2 and H_3 ($\Delta\delta$ = 0.01–0.11 ppm), a typical behavior of anion-bound NH complexes.[15] Similar, albeit smaller, changes were produced by H_b while the initially merged signals (H_a and H_6) were well resolved during the course of the titration. In this milieu, it would be worthwhile to mention that the naked-eye recognition of F^- was also found quite striking in the ^{1}H NMR titration study, which was not observed, otherwise, at relatively low concentration of **5a** (UV/Vis), manifested in a color change from yellow to orange, to red in the NMR tube (Inset: Figure S28). Aside from those of aromatic and pyrrolic protons, the upfield shifts of $\Delta\delta$ 0.21 and $\Delta\delta$ 0.024 ppm were also recognized for *meso*-methyl and silylene-methyl protons, respectively, together with the appearance of two new resonances of relatively high and very poor intensity in the alkyl region of the spectra (Figure 2B). On careful examination, the newly appeared resonances at δ 0.03 and 0.12 ppm were found identical to those of pentacoordinated and hexacoordinated fluoride on the silylene moiety (BDE; Si-F = 135 kcal mol^{-1}) as reported previously with conjugated silicon polymers in the presence of TBAF.[16] Based on these results, the plausible models for overall complexation of F^- to **5a** may be epitomized as shown in the upper panel of Figure 2B. Nevertheless, taking into account of very low intensity of hexacoordinated fluoride resonance in conjunction with ^{1}H NMR titration data such as F^--bound **5a** complex and the corresponding fitted stoichiometry of 1:2 (H:G) led us to suggest that the observed signal at δ 0.12 ppm could be an artefact, and therefore, the pentacoordination of fluoride appeared to be the most likely.

In contrast to what observed with F^-, both either the ^{1}H NMR (500 MHz) titration spectra of **5a** with CN^-, $H_2PO_4^-$, Cl^- and AcO^- or in the presence of excess of Br^-, I^-, and HSO_4^- (5 equiv each) did not cause any significant changes, either in the NH region, or in the spectrum as a whole, suggesting a remarkable selectivity of **5a** towards F^- (Figures S30–S34 in the Supporting Information).

To obtain more clarity about F^--complexation to dyad **5a**, ^{19}F NMR spectrum of TBAF was recorded in $[D_6]$DMSO solution in the presence of **5a** (Figure 3A). Originally, ^{19}F NMR spectrum of TBAF displayed a free fluoride resonance at δ −104.9 ppm.

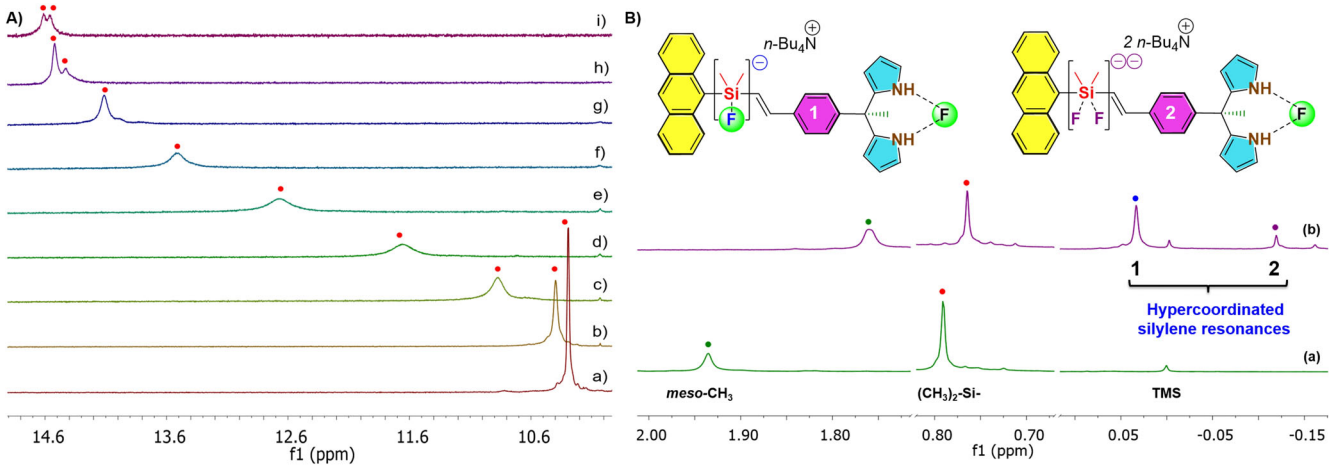


Figure 2. A) Selected region (only NHs; labelled as red dots) of ^{1}H NMR (400 MHz) spectral changes during the titration of **5a** (0.02 M) with F^- (0.2 M) in $[D_6]$DMSO at 298 K. a) **5a** only, b) **5a** + 0.33 equiv F^-, c) **5a** + 0.66 equiv F^-, d) **5a** + 1.0 equiv F^-, e) **5a** + 1.33 equiv F^-, f) **5a** + 1.66 equiv F^-, g) **5a** + 2.0 equiv F^-, h) **5a** + 2.66 equiv F^-, and i) **5a** + 4.0 equiv F^-. B) Selected alkyl regions of ^{1}H NMR (400 MHz) spectral changes during the titration of **5a** (0.02 M) with F^- (0.2 M) in $[D_6]$DMSO at 298 K. a) **5a** only and b) **5a** + 4.0 equiv F^-. The resonances of TBA are omitted for clarity.

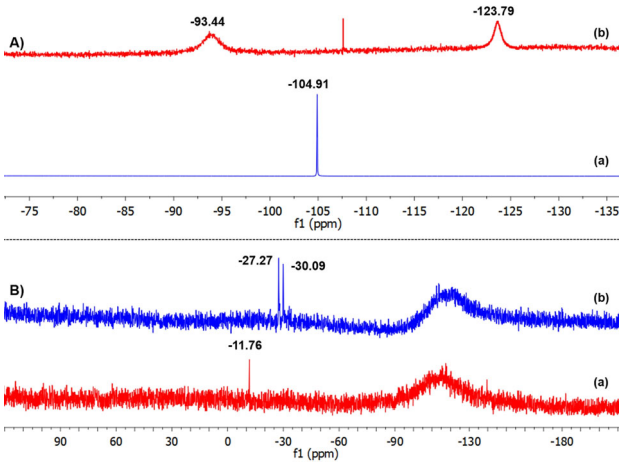


Figure 3. A) Partial ^{19}F NMR (376 MHz, [D_6]DMSO, 298 K) spectra of (a) TBAF only and (b) TBAF + 0.25 equiv **5a**. B) Partial ^{29}Si NMR (80 MHz, $CDCl_3$, 298 K) spectra of (a) **5a** only and (b) **5a** + 5.0 equiv TBAF.

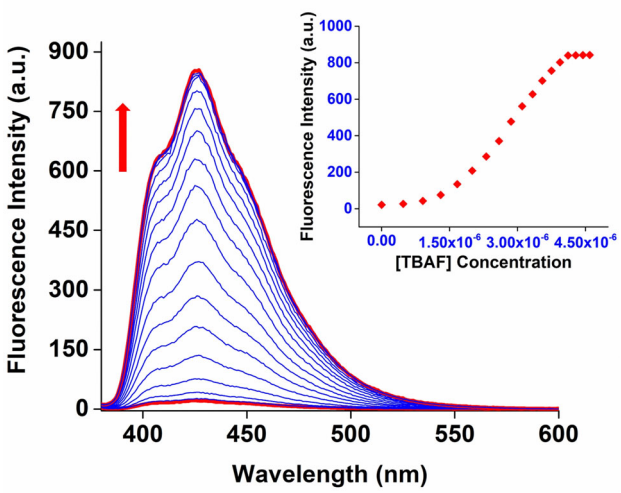


Figure 4. Fluorescence emission (titration) spectra of dyad **5a** in DCM (1 μM) upon incremental addition of TBAF. From bottom to top trace, [F^-] = 0.0, 0.476, 0.91, 1.30, 1.67, 2.0, 2.31, 2.6, 2.86, 3.10, 3.33, 3.55, 3.75, 3.94, 4.12, 4.29, 4.44 and 4.6 μM. Inset (right): changes in the emission intensity of **5a** vs. F^- concentration (λ_{ex} = 371 nm and λ_{em} = 426 nm).

The addition of **5a** (0.25 equiv) to the [D_6]DMSO solution of TBAF resulted in the appearance of two new broad resonances at δ −93.44 and −123.8 ppm in the downfield and upfield regions, respectively. Whereas a significant downfield shift of $\Delta\delta$ 11.5 ppm w.r.t. free TBAF resonance clearly indicates the participation of F^- in hydrogen bonding with NHs of dyad **5a**, an upfield shift of $\Delta\delta$ 18.9 ppm supports the generation of pentacoordinated fluoride species. In order to get an unequivocal proof about later, ^{29}Si NMR spectrum of **5a** was also recorded in the presence of TBAF. As shown in Figure 3 B (b), mixing **5a** and TBAF in $CDCl_3$ resulted in the appearance of a doublet at δ −28.68 ppm having J_{SiF} = 225.6 Hz. This observation is in agreement with those of previously reported organosilicon compounds exhibiting pentaccordination phenomena.[17,18]

Having established the multisite F^- coordination (NHs and Si) to dyad **5a**, the ^1H NMR titration result of **5a** with F^- was also examined by fluorescence spectroscopy (Figure 4). Interestingly, the incremental addition of F^- into a DCM solution of **5a** resulted in a significant enhancement of the emission intensity at λ_{em} = 426 nm. When 4.6 equiv of F^- was added, the emission intensity reached its maximum with ca. 32-fold enhancement factor. Notably, there was a linear dependence of the fluorescence intensity on the F^- concentration in the range from 1.5 to 4.0 μM (R^2 = 0.9960) with a detection limit of 1.97×10^{-7} M. Unlike ^1H NMR, the fact that a relatively much less amount of compound is required in fluorescence studies also allowed screening of **5b** with F^-. In particular, **5b** exhibited a similar fluorescence response as that of **5a** with ca. 12-fold enhancement factor (Figure S35 in the Supporting Information), and a detection limit of 2.57×10^{-7} M (R^2 = 0.9906). Interestingly, the detection limits of dyads **5** for F^- were found superior than those of recently reported chemosensors.[19,20] Though appreciable, these "Off-On" type fluorescence responses of dyads **5** are in marked contrast to CP anion sensors, which potentially function by fluorescence quenching.[21] On the basis of the "Turn-On" fluorescence responses of dyads **5**, it is reasonable to speculate that (*i*) upon binding to F^-, **5** become more planar leading to an enhanced fluorescence response[22] and/or (*ii*), and most obviously, pentaccordination of F^- to silicon significantly contributes toward fluorescence enhancement.[23]

The fluorescence titrations data of **5a** and **5b** were used to estimate quantitative binding constants and stoichiometry. In particular, the binding constants were obtained using *OpenDataFit* (*Bind Fit*) software.[24] As shown in Table 1, the best fit were obtained for 1:2 (**5**:F^-) non-cooperative model using both Nelder Mead and L-BFGS-B fit methods. In case of **5a**, both fit methods produced nearly comparable values of K_1 and K_2 and covariance of the fit (Cov_{fit}). However, Nelder Mead method was found superior over L-BFGS-B for **5b** based on the Cov_{fit}.[25] Furthermore, **5b** exhibited a higher binding affinity for F^-, which is ca. 3 order of magnitude greater than **5a**.

To conclude, herein, we introduced a hydrosilylation method that allowed a one-step synthesis of silicon-bridged functional DPMs from appropriate silane and alkynyl precursors. Notably, precursors **3** bear a structural or functional group resemblance to known CPs,[8]—a feature that we hope will reinstate hydrosilylation method as a viable avenue for the development of a new class of promising chemodosimeteric, macrocyclic and polymeric systems having a rich molecular recognition chemistry.[26,27] In accord with this latter suggestion are the findings that the introduction of silicon-bridge in the functional DPMs offered an opportunity for multi-site F^- recognition following both hydrogen bonding and pentacoordination.

Current efforts are devoted to exploring the hydrosilylation method to the more complex systems such as CPs to develop multifunctional materials with exciting applications, and the findings of these work(s) will be reported soon.

Table 1. Comparison of various models (fit method: Nelder–Mead) for binding of fluoride anion to dyads **5a** and **5b**.[a]

Binding Model	Dyad 5a			Dyad 5b		
	K_1 [M^{-1}][b] ± % error	K_2 [M^{-1}][b]	Cov_{fit}[b]	K_1 [M^{-1}][b] ± % error	K_2 [M^{-1}][b]	Cov_{fit}[b]
1:1		Fit failed			Fit failed	
1:2 (full)	$1.08\times10^6\pm82$	$2.77\times10^5\pm9.7$	0.0117	$3.60\times10^5\pm79$	$3.60\times10^5\pm79$	0.0116
1:2 (non-coop.)[c]	$1.09\times10^6\pm3.8$	2.73×10^5	0.0117	$2.90\times10^6\pm6.7$	7.25×10^5	0.0119
1:2 (non-coop.)[c,d]	$1.00\times10^6\pm3.7$	2.50×10^5	0.0117	$1.00\times10^6\pm5.8$	2.50×10^5	0.0188
1:2 (additive)	$65.6\pm51\,082$	$3.34\times10^8\pm51\,100$	0.0207	$487\pm29\,521$	$3.48\times10^8\pm29\,523$	0.0175
1:2 (statistical)		Fit failed			Fit failed	

[a] The fluorescence titration experiments were performed in DCM solvent at 20 °C. [b] Binding constants and covariance of the fit were obtained using *OpenDataFit* (*Bind Fit*) at http://supramolecular.org. [c] For non-cooperative binding K_2 was calculated as $K_2 = K_1/4$ from the K_1 value obtained. [d] Fit Method used was L-BFGS-B.

Acknowledgements

This work was supported by SERB New Delhi, Government of India (Grant YSS/2015/002036 to B. G.) under Young Scientist Scheme. B. G. is speechless to express his gratitude towards his little darling doll who made him entirely comfortable during this work with all love and support.

Conflict of interest

The authors declare no conflict of interest.

Keywords: anions · heterocycles · host-guest systems · hydrosilylation · silicon

[1] a) K. Tamao, S. Yamaguchi, M. Uchida, T. Izumizawa, K. Furukawa in *Organosilicon Chemistry, Vol. 40* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **2008**, pp. 245–251; b) P. Neugebauer, B. Jaschke, U. Klingebiel in *The Chemistry of Organic Silicon Compounds, Vol. III* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **2001**, pp. 429–467.

[2] a) S. B. J. Kan, R. D. Lewis, K. Chen, F. H. Arnold, *Science* **2016**, *354*, 1048–1051; b) B. Hidding, *Science* **2018**, *360*, 489–490; c) J. Ducharme, K. Auclair, *ChemBioChem* **2017**, *18*, 432–434; d) A. K. Franz, S. O. Wilson, *J. Med. Chem.* **2013**, *56*, 388–405; e) P.-C. Chen, Y.-N. Chen, P.-C. Hsu, C.-C. Shih, H.-T. Chang, *Chem. Commun.* **2013**, *49*, 1639–1641; f) B. König, M. Rödel, P. Bubenitschek, P. G. Jones, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 661–662; *Angew. Chem.* **1995**, *107*, 752–754; g) M. A. Brook, *Chem. Eur. J.* **2018**, *24*, 8458–8469; h) Z. Zhao, T. Jiang, Y. Guo, L. Ding, B. He, Z. Chang, J. W. Y. Lam, J. Liu, C. Y. K. Chan, P. Lu, L. Xu, H. Qiu, B. Z. Tang, *J. Polym. Sci. Part A* **2012**, *50*, 2265–2274; i) L. Gai, J. Mack, H. Lu, T. Nyokong, Z. Li, N. Kobayashi, Z. Shen, *Coord. Chem. Rev.* **2015**, *285*, 24–51.

[3] a) J. S. Lindsey, *Acc. Chem. Res.* **2010**, *43*, 300–311; b) Y. Ding, W.-H. Zhu, Y. Xie, *Chem. Rev.* **2017**, *117*, 2203–2256; c) G. I. Vargas-Zúñiga, J. L. Sessler, *Coord. Chem. Rev.* **2017**, *345*, 281–296 and references therein; d) I. Saha, J. T. Lee, C.-H. Lee, *Eur. J. Org. Chem.* **2015**, 3859–3885 and references therein.

[4] a) M. Renić, N. Basarić, K. Mlinarić-Majerski, *Tetrahedron Lett.* **2007**, *48*, 7873–7877; b) S. M. S. Chauhan, T. Bisht, B. Garg, *Sens. Actuators B* **2009**, *141*, 116–123; c) K. Muthukumaran, M. Ptaszek, B. Noll, W. R. Scheidt, J. S. Lindsey, *J. Org. Chem.* **2004**, *69*, 5354–5364; d) N. A. M. Pereira, A. Lemos, A. C. Serra, T. M. V. D. Pinho e Melo, *Tetrahedron Lett.* **2013**, *54*, 1553–1557.

[5] a) S. M. S. Chauhan, B. Garg, T. Bisht, *Supramol. Chem.* **2009**, *21*, 394–400; b) E. Mulugeta, R. Dutta, Q. He, V. Lynch, J. Sessler, C.-H. Lee, *Eur. J. Org. Chem.* **2017**, 4891–4895; c) B. Garg, T. Bisht, S. M. S. Chauhan, *New J. Chem.* **2010**, *34*, 1251–1254; d) G. Bruno, G. Cafeo, F. H. Kohnke, F. Nicolò, *Tetrahedron* **2007**, *63*, 10003–10010; e) K.-C. Chang, T. Minami, P. Koutnik, P. Y. Savechenkov, Y. Liu, P. Anzenbacher, Jr., *J. Am. Chem. Soc.* **2014**, *136*, 1520–1525; f) A. S. F. Farinha, A. C. Tomé, J. A. S. Cavaleiro, *Tetrahedron Lett.* **2010**, *51*, 2184–2187; g) B. Garg, T. Bisht, S. M. S. Chauhan, *J. Inclusion Phenom. Macrocyclic Chem.* **2011**, *70*, 249–255.

[6] a) B. Marciniec, J. Gulinski, W. Urbaniak, Z. W. Kornetka in *Comprehensive Handbook on Hydrosilylation* (Eds.: B. Marciniec), Pergamon Press, Oxford, **1992**, pp. 754; b) B. Marciniec in *Hydrosilylation* (Eds.: B. Marciniec), Springer Netherlands, Dordrecht, **2009**, pp. 53–86; c) J. C. Sanchez, W. C. Trogler, *Macromol. Chem. Phys.* **2008**, *209*, 1527–1540; d) P. Lu, J. W. Y. Lam, J. Liu, K. K. W. Jim, W. Yuan, N. Xie, Y. Zhong, Q. Hu, K. S. Wong, K. K. L. Cheuk, B. Z. Tang, *Macromol. Rapid Commun.* **2010**, *31*, 834–839.

[7] a) F. Ebner, L. Greb, *J. Am. Chem. Soc.* **2018**, *140*, 17409–17412; b) T. Tanaka, A. Osuka, *Chem. Commun.* **2015**, *51*, 8123–8125.

[8] V. Valderrey, E. C. Escudero-Adán, P. Ballester, *J. Am. Chem. Soc.* **2012**, *134*, 10733–10736.

[9] L. Adriaenssens, G. Gil-Ramírez, A. Frontera, D. Quiñonero, E. C. Escudero-Adán, P. Ballester, *J. Am. Chem. Soc.* **2014**, *136*, 3208–3218.

[10] C. D. Kumar, K. Sirisha, D. K. Dhaked, P. Lokesh, A. V. S. Sarma, P. V. Bharatam, S. Kantevari, P. Sripadi, *J. Org. Chem.* **2015**, *80*, 1746–1753.

[11] Earlier efforts to perform Sonogashira coupling of 5-(4-bromophenyl) DPM with TMS-acetylene in TEA-THF system at RT proved unsuccessful, resulting in the recovery of starting material. Additional refinements such as Lindsey's protocol [4c] furnished 5-(4-ethynylphenyl) DPM in poorer yield, and was found insufficient to examine hydrosilylation reaction.

[12] Our initial attempts, where we used NaI, THF/toluene (high dilution), shorter reaction time, and low temperature (< 80 °C) either met with no success or furnished desired compound (**5a**) in very low concentration as monitored by qualitative TLC analysis. For more details; see Table S1.

[13] R. Nishiyabu, P. Anzenbacher, Jr., *Org. Lett.* **2006**, *8*, 359–362.

[14] R. Montis, A. Bencini, S. J. Coles, L. Conti, L. Fusaro, P. A. Gale, C. Giorgi, P. N. Horton, V. Lippolis, L. K. Mapp, C. Caltagirone, *Chem. Commun.* **2019**, *55*, 2745–2748.

[15] B. Garg, T. Bisht, S. M. S. Chauhan, *Sens. Actuators B* **2012**, *168*, 318–328.

[16] G. Kwak, M. Fujiki, T. Masuda, *Macromolecules* **2004**, *37*, 2422–2426.

[17] H. Lenormand, J.-P. Goddard, L. Fensterbank, *Org. Lett.* **2013**, *15*, 748–751.

[18] N. Kano, F. Komatsu, M. Yamamura, T. Kawashima, *J. Am. Chem. Soc.* **2006**, *128*, 7097–7109.

[19] R. Sedghi, H. Javadi, B. Heidari, A. Rostami, R. S. Varma, *ACS Omega* **2019**, *4*, 16001–16008.

[20] M. K. Salomón-Flores, I. J. Bazany-Rodriguez, D. Martinez-Otero, M. A. Garcia-Eleno, J. J. Guerra-Garcia, D. Morales-Morales, A. Dorazco-Gonzaleza, *Dalton Trans.* **2017**, *46*, 4950–4959.

[21] a) H. Miyaji, P. Anzenbacher, Jr., J. L. Sessler, E. R. Bleasdale, P. A. Gale, *Chem. Commun.* **1999**, 1723–1724; b) P. Anzenbacher, Jr., K. Jursíková, J. L. Sessler, *J. Am. Chem. Soc.* **2000**, *122*, 9350–9351.

[22] G. Xu, M. A. Tarr, *Chem. Commun.* **2004**, 1050–1051.

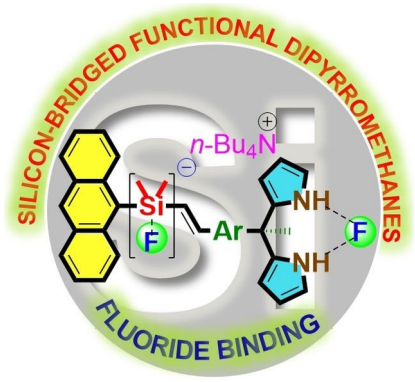
[23] S. Yamaguchi, S. Akiyama, K. Tamao, *J. Am. Chem. Soc.* **2000**, *122*, 6793–6794.

[24] a) http://supramolecular.org; b) P. Thordarson, *Chem. Soc. Rev.* **2011**, *40*, 1305 – 1323; c) D. Brynn Hibbert, P. Thordarson, *Chem. Commun.* **2016**, *52*, 12792 – 12805.
[25] The results of the calculations can be found at a) http://app.supramolecular.org/bindfit/view/51dd87c8-39ce-4160-b820-11d6777f3015; b) http://app.supramolecular.org/bindfit/view/c8ca64ad-9148-4da0-8274 – 550501f4e266.
[26] L. L. Zhao, X.-S. Yang, H. Chong, Y. Wang, C.-G. Yan, *New J. Chem.* **2019**, *43*, 5503 – 5511.
[27] X. Wu, H. Wang, S. Yang, H. Tian, Y. Liu, B. Sun, *ACS Omega* **2019**, *4*, 4918 – 4926.

Manuscript received: October 10, 2019
Revised manuscript received: November 18, 2019
Version of record online: ■■ ▮▮, 0000

COMMUNICATION

In hyperspace: Silylene-spaced functional dipyrromethanes are synthesized using a hydrosilylation approach and discovered as selective fluoride sensors following hydrogen-bonding and hypercoordination phenomena.



Bhaskar Garg, Tanuja Bisht, Yong-Chien Ling*

■■ – ■■

A Hydrosilylation Approach to Silicon-Bridged Functional Dipyrromethanes: Introducing Silicon to A New Arena