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Silicon–oxygen-bonded oligomers having thermoelectric switching properties

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The electrical properties of siloxane oligomers prepared from the reaction of 1,4-naphthalenediol or 1,4-naphthoquinone with diphenylsilane using different palladium catalysts, such as $PdCl_2$, $Pd(TMEDA)Cl_2$, $Pd(TEEDA)Cl_2$ (where TMEDA = *N,N′*-tetramethylethylenediamine, TEEDA = *N,N′*-tetraethylethylenediamine), are dependent on the catalyst. Thermoelectric switching properties can be obtained from the siloxane prepared from the coupling reaction of diphenylsilane with 1,4-naphthoquinone or 1,4-naphthalenediol using $Pd(TMEDA)Cl_2$ as catalyst. Copyright © 2001 John Wiley & Sons, Ltd.

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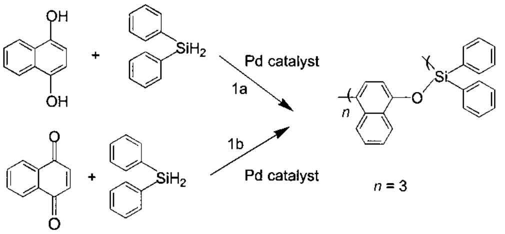
INTRODUCTION

Cyclic compounds having multiple aromatic rings, such as calixarene, possess π-interactions and also have capabilities for π–cation interaction.[1,2] Crown ethers also bind to cations and recognize molecules.[3,4] Cyclic siloxanes are also useful in molecular recognition[5–7] and possess properties similar to crown ethers.[8] The siloxanes are usually prepared by substitution reactions on silicon—halogen-bonded compounds,[9,10] dehydrogenative coupling reactions[11] or by reductive coupling reactions of carbonyl compounds with silanes.[12] Dehydrogenative coupling and reductive coupling reactions are catalysed by different metal catalysts.[13–18] Catalytic methods are extensively used in the Si—O-bonded oligomers and palladium catalysts are found to be superior in these reactions.[19] Silicon can form direct metal—silicon bonds[20] and they also form complexes with transition metals through Si—O—metal bonds.[21] There is also a need to understand the products from transition-metal-catalysed reactions of silicon substrates leading to metallacycles.[22] Silicon can expand its valency and can possess five, six or four co-ordination depending on its environment.[23–25] Siloxanes having polynuclear aromatic rings on the main chain are expected to produce interactions through π-stacking. These weak interactions could lead to supramolecular assemblies having novel physicochemical properties.[26] Such properties should be susceptible to thermal effects. This work is concerned with synthesis of siloxanes containing naphthalonic units on the main chain and their thermal properties.

We have recently demonstrated that palladium catalysts are suitable for synthesis of siloxane oligomers.[12] We have extended this to dehydrogenative coupling reactions between diphenylsilane with 1,4-naphthalenediols or with 1,4-naphthoquinone with catalysts such as $PdCl_2$, $Pd(TMEDA)Cl_2$, $Pd(TEEDA)Cl_2$ (where TMEDA = *N,N′*-tetramethylethylenediamine, TEEDA = *N,N′*-tetraethylethylenediamine) (Eqn [1]).



[1]

The M_n values of the oligomers are in the range 3800–4000 with a polystyrene standard. The oligomers are soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, etc. These oligomers are devoid of Si—H frequencies but possess ν_{OH} frequencies. The Si—

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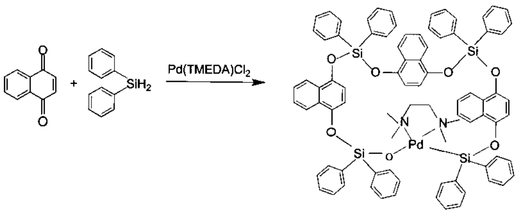
O frequencies in each of these oligomers appear as strong multiple absorptions in the region 1000—1100 cm^{-1}. The IR spectra of the oligomers are similar except in the region 1600—1700 cm^{-1}, where the ν_{OH} overtone vibration occurs. The siloxanes have palladium attached to them. To determine the end group present in the product a representative fast atom bombardment (FAB) mass spectrum of the product obtained from the reaction of 1,4-naphthoquinone with diphenylsilane catalysed by Pd(TMEDA)Cl_2 shows it to have the structure **I** (Eqn [2]).



[2]

I

The highest *m/z* value in the FAB mass spectrum of **I** is at 1439 and corresponds to four units of diphenylsilane and three naphthalenic units with palladium(II) attached to tetramethylethylenediamine. The *m/z* signal at 1439 is a broad spread from 1436–1444 due to the isotopic abundance of palladium. In **I** the palladium is anchored through Si—O—Pd and Si—Pd bonds. These bonds might have formed during the coupling reactions that follow oxygenation of silanes from contaminated water. Examples of such reactions are well documented.[27] The mass spectra could be due to the degradation of the oligomers and may occur due to colloidal palladium formed during the coupling reaction, and trapped in the stacks of the siloxane oligomers.[28,29] Colloidal metal formation during dehydrogenative coupling reactions is well documented. The palladium atoms thus deposited may be responsible for the molecular mass and the FAB mass spectrum. Although in the case of the reaction of diphenylsilane with naphthoquinone catalysed by Pd(TMEDA)Cl_2 it has not been possible to obtain an NMR signal from the TMEDA moiety in solution, it is likely that the palladium is loosely bound and precipitates out of the solution.

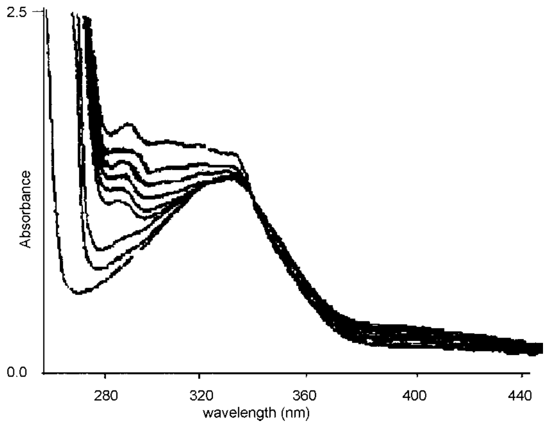


Figure 1 Change in absorbance during the reaction of 1,4-naphthalenediol (0.1 mmol) with diphenylsilane (0.1 mmol) in the presence of Pd(TMEDA)Cl_2 (0.01 mmol) in dichloromethane (3.5 cm^3) recorded at 4 min time intervals at 30 °C.

The visible spectra of a mixture containing 1,4-naphthalenediol with diphenylsilane in the presence of Pd(TMEDA)Cl_2 changes with time and shows an isosbestic point at 335 nm (Fig. 1), whereas a similar study on the reaction of diphenylsilane and 1,4-naphthoquinone with Pd(TMEDA)Cl_2 shows two isosbestic points, one at 370 nm and another at 335 nm (Fig. 2). The observation of a common isosbestic point at 335 nm in the two independent reactions indicates that these reactions pass through a common intermediate. The isosbestic point at 335 nm is related to the Si—O bond formation, whereas the isosbestic point at 370 nm occurs due to the reductive process of naphthoquinone (path B of Scheme 1). The final products obtained from these reactions are diamagnetic (*vide* ESR) and no radical is observed during the course of these reactions. As both the reactions pass through a common intermediate, the favoured reaction mechanism in these cases is the one involving oxidative addition and reductive elimination (Scheme 1). In

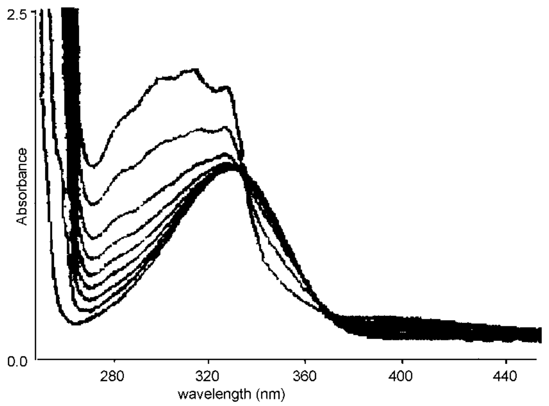
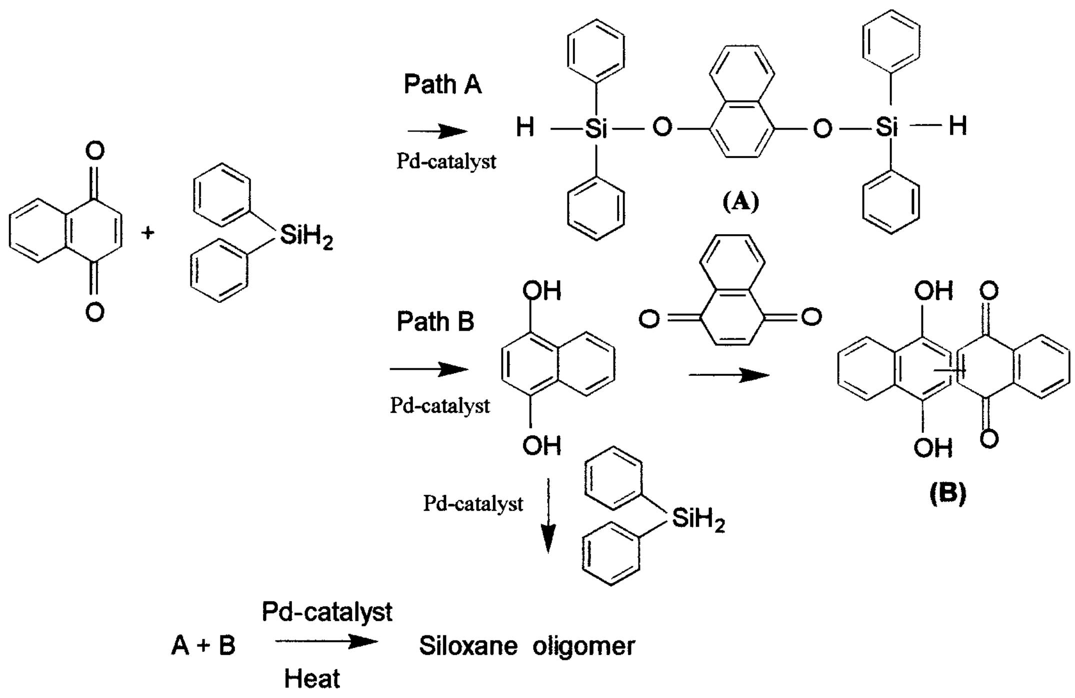


Figure 2 Change in absorbance during the reaction of 1,4-naphthoquinone (0.1 mmol) with diphenylsilane (0.1 mmol) in the presence of Pd(TMEDA)Cl_2 (0.01 mmol) in dichloromethane (3.5 cm^3) recorded at 4 min time intervals at 30 °C.



Scheme 1

the naphthoquinone reduction reaction the absorption maximum at 333 nm is assigned to a charge transfer complex (**B**) that can be formed by interaction of partially reduced naphthoquinone with naphthalenediol, of which the latter is formed by reduction of a metal hydride species during the reaction. The charge transfer complex **B** can participate in the polymerization reaction. Thus, the pathways in these reactions are different than the pathways involved in the Ge—O bond-forming reaction by cross-coupling of germylene with quinonic compounds (where it occurs through radical mechanism).[30]

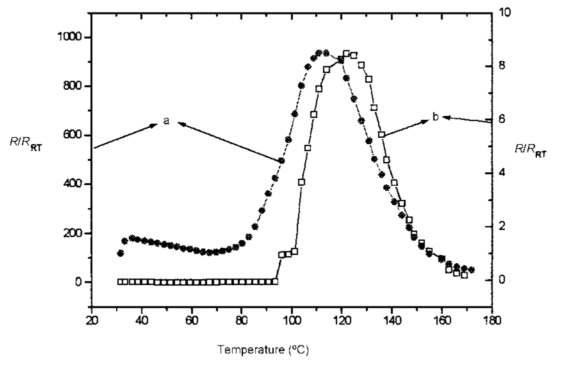


Figure 3 Plot of resistance R normalized to resistance at room temperature R_{RT} versus temperature of the siloxane prepared by Pd(TMEDA)Cl_2 catalyst from the reaction of (a) 1,4-naphthalenediol and (b) 1,4-naphthoquinone with diphenylsilane.

An intriguing feature of these oligomers is that siloxane films prepared by different catalysts have different shapes for variation of resistance versus temperature. The profiles obtained from each reaction are shown in Figs 3 and 4. As the temperature increases the resistance offered by the siloxane prepared by the $PdCl_2$ catalyst decreases (Fig. 3b) continuously. It has a resistance versus temperature profile similar to a semiconductor. In the case of the Pd(TMEDA)Cl_2 and Pd(TEEDA)Cl_2 catalysts the resistance passes through a maximum with increase in temperature (Figs 3a and 4a). We defined the property of thermoelectric switching as one where a plot of resistance versus temperature has a normal Gaussian shape. Such properties were observed in systems having a combination of proton conductivity with inherent semiconducting properties, radical conductivity and structural changes around the metal ion.[31–35] Understanding such phenomena at the molecular level requires a thorough study on structure–property correlations. Moreover, the class

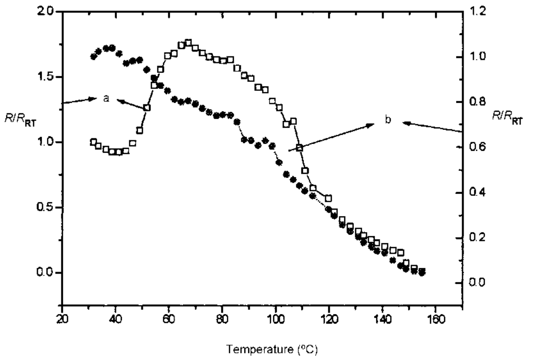


Figure 4 Plot of resistance R normalized to resistance at room temperature R_{RT} versus temperature of the siloxane prepared from the reaction of 1,4-naphthoquinone with diphenylsilane by (a) Pd(TEEDA)Cl_2 and (b) $PdCl_2$ as catalyst.

of oligomers under consideration have sp^2-hybridized C—O bonds attached to silicon. These can impart delocalization in the system through involvement of d-orbitals of silicon as well as the lone pair of electrons on oxygen. These siloxanes are prepared from dehydrogenative coupling or reductive coupling reactions with the catalyst derived from the same metal. Thus, the difference in the resistance versus temperature plots of the films indicates the property originates from the environment of the metal ion. The IR spectra of siloxanes prepared from 1,4-naphthoquinone with diphenylsilane by Pd(TMEDA)Cl_2 and $PdCl_2$ have a clear difference in the regions 3400 and 1680 cm^1 due to —OH stretching and overtone absorptions (Fig. 5a and b). The sample showing the property of thermoelectric switching possesses relatively higher intense absorptions at these positions, suggesting recognition/absorption of water in the interstices. A considerable decrease in the intensity of absorption peaks of **I** on heating to 150 °C (Fig. 5b and c) is observed. It is worth noting that a freshly prepared sample on heating to 180 °C does not show the same path of resistance versus temperature. Further proof of the loss of water molecules during heating from 30 to 180 °C is supported by thermogravimetry (TG), where the siloxanes prepared from 1,4-naphthoquinone and diphenylsilane by $PdCl_2$, Pd(TMEDA)Cl_2 and Pd(TEEDA)Cl_2 have losses of weight of 0%, 1.5% and 3.7% respectively. Differential scanning calorimetry (DSC) of the samples shows an endothermic process at the temperature where the resistance reaches maximum values. Thus the effect is attributed to the inclusion of water molecules in the interstices of the lattice.

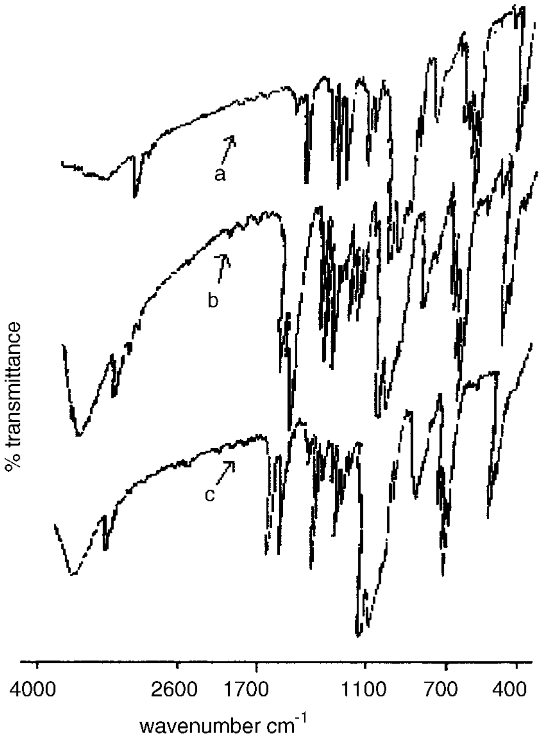


Figure 5 IR (KBr) spectra of siloxane prepared by (a) $PdCl_2$ (b) Pd(TMEDA)Cl_2. (c) IR spectra of **I** heated to 150 °C.

The loss of a water molecule changes the environment around the palladium and results in a decrease in resistance from a limiting temperature. A change of co-ordination geometry of d^8-complexes has recently been used in a fluorescence thermometer device.[36] To obtain qualitative information on the geometrical change occurring around the palladium, a far-IR spectra of **I** was recorded at room temperature and after heating to 200 °C. In both cases there are strong absorptions at 517 and 488 cm^{-1}, and this remains unchanged on heating. These bands are attributed to the Si—O framework on the basis of orthosilicate examples.[37] The only change observed is on a weak absorption appearing at 418 cm^{-1}; this absorption splits into two absorptions at 418 and 405 cm^{-1}. This qualitatively supports the proposal of a change of co-ordination around palladium. Thus, it is believed that the irreversible effect of the thermoelectric switching property originates on the change of geometry around palladium, which is embedded in the siloxane network. Use of ethylenediamine controls the pore size in a supramolecular assembly of tin phosphates.[38–40] The cavity shapes and sizes in the porous molecules are controlled by use of quaternary ammonium salts.[39,40]

The oligomers under consideration are thermally unstable. They decompose on heating, and a continuous weight loss in the region 180–800 °C is observed in each case. However, they have good thermal stability in the range 30–180 °C. The continuous weight loss indicates hydrolytic cleavage of Si—O bonds to give smaller molecular weight products.

In conclusion, new oligomers having provision for sp^2 C—O bonds attached to silicon and possessing the property of thermoelectric switching are described.

EXPERIMENTAL

The $PdCl_2$ TMEDA, diphenylsilane, 1,4-naphthoquinone, and 1,4-naphthalenediols were obtained from Aldrich (USA) and were used without further purification. The IR spectra were recorded on a Nicolet-416 FT-IR spectrophotometer, the far-IR on a BOMEM DA-8 spectrophotometer, and the UV–visible spectra on a Hitachi U-2001 spectrophotometer; DSC and TG were undertaken using a Metler Toledo Star system. The molecular weights of the oligomers were determined in THF using a Water GPC-HPLC-600 instrument. The ^{1}H NMR were recorded on a Bruker 400 MHz NMR spectrometer. The resistance of the samples was measured on films made on a mica plate by using a set up comprising of a Hewlett Packard 34401 multimeter, a Keithley 6512 programmable electrometer and an Agronics 93-C DC power supply unit. The films were prepared by dissolving 2 mg of the oligomers in acetone (0.5 cm^3) and then spreading over a mica plate with the aid of a capillary tube and drying by an air drier.

Coupling reaction of 1,4-naphthoquinone with diphenylsilane by Pd(TMEDA)Cl_2

A paste was made by mixing 1,4-naphthoquinone (79 mg, 0.5 mmol) with diphenylsilane (81 mg, 0.5 mmol) in a Schlenck tube and to this Pd(TMEDA)Cl_2 (9 mg 0.037 mmol) was added and put in an oil bath at 90 °C for 2 h. The black mass obtained was washed with hexane ($3 \times 10\,cm^3$) and the residue thus obtained was dried under vaccuum; yield 46 mg (65%) of siloxane (**I**). ^{1}H NMR ($CDCl_3$) 6.2–8.4 (m,58H), 1.8 (m, 16H). Elemental analysis: Found: C, 70.45; H, 4.98. Calc. for $C_{84}H_{74}N_2O_7PdSi_2$: C, 70.09; H, 5.29%. Mass (*m/z*) 1445–1437, 1352, 1237, 1154, 1098, 1075, 1016, 956, 937, 896, 878, 840, 814, 787, 758, 697, 676, 637, 619, 577, 559, 521. IR (KBr) 3360(bs), 1618(s), 1590(s), 1550(s), 1420(s), 1390(s), 1350(s), 1230(s), 1200(s), 1090(s), 1040(s), 870(bs), 720(s), 700(s), 680(s), 660(s), 480(s).

A similar reaction of 1,4-naphthoquinone with diphenylsilane in the presence of $PdCl_2$ and Pd(TEEDA)Cl_2 gave to corresponding siloxanes in 32% and 40% yields respectively.

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REFERENCES

1. Ma JC, Dougherty DA. *Chem. Rev.* 1997; **97**: 1303.
2. Ikeda A, Shinkai S. *Chem. Rev.* 1997; **97**: 1713.
3. Gokel GW. *J. Chem. Soc. Chem. Commun.* 2000; **1**.
4. Kimura K, Mizutani R, Yokoyama M, Arakawa R, Matsubayashi G-E, Okamoto M, Doe H. *J. Am. Chem. Soc.* 1997; **119**: 2062.
5. Procopio LJ, Berry DH. *J. Am. Chem. Soc.* 1991; **113**: 4039.
6. Bedard TC, Corey JY. *J. Organomet. Chem.* 1992; **428**: 315.
7. Lickiss PD, *Advances in Inorganic Chemistry*, vol. 42, Sykes AG (ed.). Academic Press: San Diego, CA, 1995; 147–262.
8. Lorentz C, Schubert U. *Chem. Ber.* 1995; **128**: 1267.
9. Maciejewski M. *J. Macromol. Sci. Chem.* 1979; **A13**: 77.
10. Maciejewski M, Gwizdowski A, Peczak P, Pietrzak A. *J. Macromol. Sci. Chem.* 1981; **A16**: 441.
11. Lorentz C, Schubert U. *Chem. Ber.* 1995; **128**: 1267.
12. Purkayastha A, Baruah JB. *Appl. Organomet. Chem.* 2000; **14**: 477.
13. Lukevics E, Dzintara M. *J. Organomet. Chem.* 1985; **295**: 265.
14. Armitage DA, Corriu RJP, Kendrick TC, Prabhoo B, Tilley TD, White JW, Young JC. *The Silicon Heteroatom Bond.* Wiley: New York, 1991.
15. Baruah JB, Osakada K, Yamamoto T. *J. Mol. Catal.* 1995; **101**: 17.
16. Baruah JB, Osakada K, Yamamoto T. *Organometallics* 1996; **15**: 456.
17. Baruah JB. *Polyhedron* 1996; **15**: 3709.
18. Baruah JB, Osakada K. *Main Group Metal Chemistry* 1997; **20**: 661.

19. Iswakura Y, Uno K, Toda F, Hattori K, Abe M. *Bull. Chem. Soc. Jpn.* 1971; **44**: 1400.
20. Corey JY, Braddock-Wilking J. *Chem. Rev.* 1999; **99**: 1758.
21. Abbenhuis HCL, Vorstenbosch MLW, Vansaten RA, Smeets WJJ, Spek AL. *Inorg. Chem.* 1997; **36**: 6431.
22. Breliere C, Corriu RJP, Royo G, Wong WWC, Zwelker J. *Organometallics* 1990; **9**: 2633.
23. Atwood JL, Davies JED, MacNicol DD, Vogtle F. (eds). *Comprehensive Supramolecular Chemistry*. Pergamon: New York, 1996.
24. Chandross EA, Miller RD. *Chem. Rev.* 1999; **99**: 1641.
25. Storhoff JJ, Mirkin CA. *Chem. Rev.* 1999; **99**: 1849.
26. Iswakura Y, Uno K, Toda F, Hattori K, Abe M. *Bull. Chem. Soc. Jpn.* 1971; **44**: 1400.
27. Matarasso-Tchiroukhire E. *J. Chem. Soc. Chem. Commun.* 1990; 681.
28. Lewis LN, Lewis N. *Chem. Mater.* 1989; **1**: 106.
29. Lewis LN. *J. Am. Chem. Soc.* 1990; **112**: 5990.
30. Kobayashi S, Iwata S, Abe M, Shoda S-I. *J. Am. Chem. Soc.* 1995; **117**: 2187.
31. Puzari A, Handique JG, Purkayastha A, Baruah JB, Srinivasan A. *Indian J. Chem.* 1999; **38A**: 521.
32. Puzari A, Baruah JB. *J. Mol. Catal.* 2000; **153**: 1.
33. Puzari A, Srinivasan A, Baruah JB. *Reactive Functional Polym.* 2000; **44**: 201.
34. Purkayastha A, Baruah JB. *New J. Chem.* 1999; **12**: 1141.
35. Puzari A, Baruah JB. *J. Org. Chem.* 2000; **65**: 2344.
36. Engeser M, Fabbrizzi L, Licchelli M, Sacchi D. *J. Chem. Soc. Chem. Commun.* 1999; 1191.
37. Nyquist RA, Kagel KO. *Handbook of Infrared and Raman Spectra of Inorganic Compounds and Organic Salts*, vol. 4. Academic Press: New York, 1997.
38. Rao CNR. *Bull. Mater. Sci.* 1999; **22**: 141.
39. Rao CNR, Gopalakrishnan J. *New Directions in Solid State Chemistry*. Cambridge University Press: Cambridge, 1997.
40. Ayyappan S, Bu X, Cheetham AK, Natarajan S, Rao CNR. *J. Chem. Soc. Chem. Commun.* 1998; 2181.