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impurity at levels as low as a few ppb.

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Theoretical Studies on the Nonlinear Optical Properties of Conjugated Homologues of Hetero-TCNQ(X=O, S, Se)

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A large number of π-conjugated polymers which exhibit fast response times and large optical nonlinearities have attracted much attention. It has been recognized that intramolecular electronic polarizations remakably contribute to the enhancement of nonlinear polarizabilities.[1-8] The conductive polymers, such as polyacethylene and polydiacetylenes, show the largest third-order nonlinear optical susceptibility $\chi^{(3)}$ among the organic materials. However, these values are too small to permit in the optical applications. Another possible origin of nonlinear optical polarizabilities in a supermolecular electronic polarization system have been studied by Meff *el al..*[9] A supermolecular electronic polarization system has
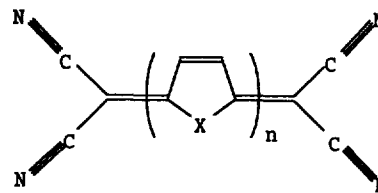
(a) X = S ;   (b) X = O ;   (c) X = Se

Figure 1. Structures of hetero-TCNQ(X=S, O, or Se).

not yet been systemetically investigated. Organic charge transfer complexes systems, such as TXF$-$TCNQ(X=S, Se, Te), are well known for a supermolecular electronic polarization system. The extensively conjugated homologues of hetero-TCNQ(Figure 1, X=O, S, Se) have been attracted as potential electron acceptors for organic conductors. Thiophene- and selenophene-TCNQs were synthesized by Gronowitz and Uppstrom in 1974[10] and have been known as the first heteroquinonoid isologues of TCNQ. Figure 1 shows the hetero- TCNQ(X=O, S, Se) structures.

Ab intio calculations of γ in the static field for regular polyenes have been carried out by Hurst *et al..*[11] Zhao *et al.*[12] and Beljonne *et al.*[13] have demonstrated large third-order hyperpolarizabilities in thiophene oligomers. It has been reported that the mixed stack of tetracyanoquinodimethane (TCNQ) with perylene exhibits large γ values.[14]

In this study, frequency dependent nonlinear optical properties of conjugated homologues of hetero-TCNQ are calculated by the use of time-dependent Hartree-Fock mothods combined with semiempirical PM3[15] calculations. The hetero-TCNQ(X=O, S, Se) systems have planar structures with all quinoid structures. All the structures were fully optimized, and have all positive vibrational frequencies. Thus, at least, these should be at the local minima of the energy hypersurface.

In this study, the time-dependent Hartree-Fock treatment of nonlinear optical propeties for perturbations made up of a static electric field and an oscillating field presented Karna *et al.*[16] is used. The energy $E(E)$ of a molecular system perturbed by an external electric field E can be written as:

$$E(E)=E^0-\mu_a E^a-(2!)^{-1}\alpha_{ab}E^a E^b-(3!)^{-1}\beta_{abc}E^a E^b$$
$$E^c-(4!)^{-1}\gamma_{abcd}E^a E^b E^c E^d-\cdots, \qquad (1)$$

where the indices a, b, c, d, and so on indicate x, y, and z. In the above equation, μ_a is the a component of the dipole moment and α_{ab}, β_{abc}, and γ_{abcd} are the components of polarizability, second-order hyperpolarizability, and third-order hyperpolarizability tensors, respectively. A component of the total dipole moment P^a is obtained from the first derivative $(\partial E(E)/\partial E^a)$, so that from Eq. (1)

$$P^a=-\mu_a-\alpha_{ab}E^b-(2!)^{-1}\beta_{abc}E^b E^c-(3!)^{-1}\gamma_{abcd}E^b E^c E^d-\cdots \quad (2)$$

Hurst *et al.*[11] fitted the electronic properties as a function of the second order of n^{-1}. In this study, α, β, and γ values for infinitely long polymeric hetero cyclic rings are estimated by the following extrapolation procedure, as

$$\log A(n)=a_0+a_1/n+a_2/n^2+a_3/n^3, \qquad (3)$$

where n is the number of the hetero cyclic ring unit and

Table 1. The PM3-predicted Electrical Properties (α, β, γ in a.u.)

(a) Thiophene-TCNQ

	freq. (eV)	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=\infty$
α	0.0	164.04	284.97	434.49	607.16	790.86	1003.14	1219.03	1443.01	1673.34	3015
	0.25	164.7	286.83	438.4	614.0	801.11	1018.26	1239.32	1469.0	1705.47	3079
	0.5	166.71	292.63	450.77	635.89	834.2	1067.55	1305.9	1554.76	1812.07	3741
	0.75	170.26	303.2	473.9	677.81	898.68	1165.71	1440.65	1730.86	2033.68	3923
	1.5	195.3	392.06	706.84	1187.5	1823.6	2975.48	4584.5	7045.34	10880.73	21447
β	0.0	483.89	–	1054.8	–	1100.6	–	1681.01	–	1883.86	4011
	0.25	502.96	–	1121.02	–	1177.85	–	1830.01	–	2009.17	4254
	0.5	569.81	–	1375.67	–	1499.35	–	2493.35	–	2828.83	6386
γ	0.0	9.02E4	5.06E5	1.77E6	4.48E6	8.85E6	–	–	–	–	3.7E7
	0.25	9.93E4	5.90E5	2.16E6	5.68E6	1.05E7	–	–	–	–	4.3E7
	0.5	1.38E5	1.03E6	4.67E6	–	–	–	–	–	–	–

(b) Furan-TCNQ

	freq. (eV)	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=\infty$
α	0.0	148.38	248.52	374.21	520.87	675.64	862.89	1051.47	1247.81	1451.09	–
	0.25	148.93	250.01	377.36	526.46	684.12	875.63	1068.79	1270.23	1479.08	2680
	0.5	150.59	254.64	387.29	544.26	711.31	916.96	1125.38	1343.94	1571.67	2867
	0.75	153.51	262.98	405.63	577.92	763.69	998.37	1238.77	1493.88	1762.58	3255
	1.5	173.85	328.58	574.55	944.65	1428.39	2292.66	3471.50	5217.60	7888.91	15554
β	0.0	374.97	–	1146.91	–	1462.66	–	2092.41	–	2379.65	4591
	0.25	386.92	–	1213.21	–	1562.72	–	2270.54	–	2602.89	5121
	0.5	427.53	–	1460.63	–	1965.64	–	3044.57	–	3627.82	7712
γ	0.0	7.17E4	3.56E5	1.23E6	3.16E6	6.42E6	–	–	–	–	2.7E7
	0.25	7.85E4	4.11E5	1.48E6	3.96E6	8.27E6	–	–	–	–	3.5E7
	0.5	1.06E5	6.77E5	2.96E6	9.58E6	–	–	–	–	–	–

(c) Selenophene-TCNQ

	freq. (eV)	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=\infty$
α	0.0	160.79	272.82	403.65	548.55	703.48	864.71	1031.22	1201.37	1374.09	2407
	0.25	161.36	274.45	406.37	552.95	709.88	873.34	1042.28	1215.00	1390.41	2439
	0.5	163.09	278.69	414.90	566.82	730.12	900.77	1077.55	1258.61	1442.76	2540
	0.75	166.14	286.65	430.46	592.47	767.99	952.55	1144.62	1342.07	1543.46	2735
	1.5	187.07	348.38	564.04	833.20	1151.83	1515.12	1918.84	2358.78	2829.93	5325
β	0.0	127.72	–	299.20	–	318.33	–	344.19	–	371.76	503
	0.25	132.42	–	313.35	–	344.11	–	358.88	–	387.31	517
	0.5	149.56	–	367.79	–	389.23	–	416.51	–	450.42	602
γ	0.0	8.95E4	4.45E5	1.34E6	2.96E6	5.38E6	–	–	–	–	2.07E7
	0.25	9.79E4	5.10E5	1.59E6	3.58E6	6.61E6	–	–	–	–	2.58E7
	0.5	1.33E5	8.25E5	2.92E6	7.31E6	–	–	–	–	–	–

$A(n)$ is the asymptotic values (for $n=\infty$).

The PM3 calculated the polarizabilities, second-, and third-order hyperpolarizabilities values for thiophene-, furan-, and selenophene-TCNQ are listed in Table 1. We expect that the PM3 values of α for the frequencies of 0.0 eV, 0.25 eV, 0.5 eV, 0.75 eV and 1.5 eV are thiophene-TCNQ(a) $\sim$3015, $\sim$3079, $\sim$3741, $\sim$3923, and $\sim$21447 *a.u.*, furan-TCNQ(b) $\sim$2624, $\sim$2680, $\sim$2867, $\sim$3255, and $\sim$15554 *a.u.*, seleno-

phene-TCNQ(c) $\sim$2407, $\sim$2439, $\sim$2539, $\sim$2735, and $\sim$5325 *a.u.*, repectively, while the PM3 values of β for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are thiophene-TCNQ(a) $\sim$4011, $\sim$4524, and $\sim$6386 a.u., furan-TCNQ(b) $\sim$4591, $\sim$5121, and $\sim$7712 a.u., selenophene-TCNQ(c) $\sim$4591, $\sim$5121, and $\sim$7712 a.u., repectively. The PM3-predicted asymptotic values of γ for the frequencies of 0.0 eV and 0.25 eV are thiophene-TCNQ(a) $\sim$3.7 e7 and $\sim$4.3 e7 a.u., furan-TCNQ
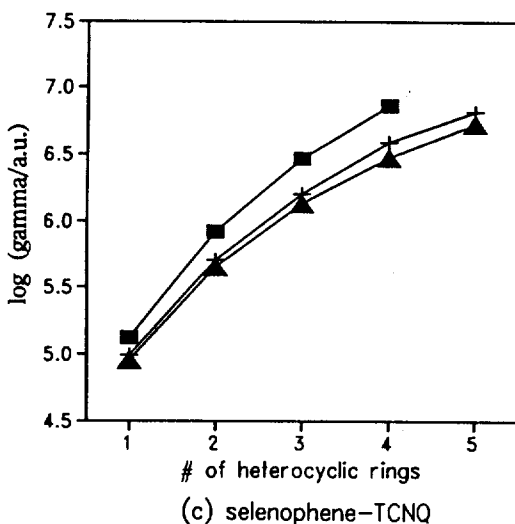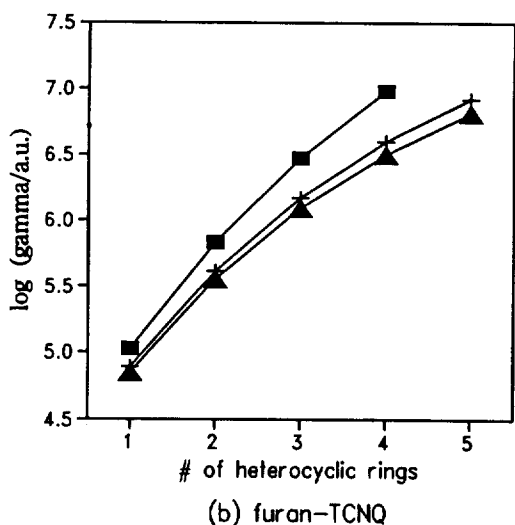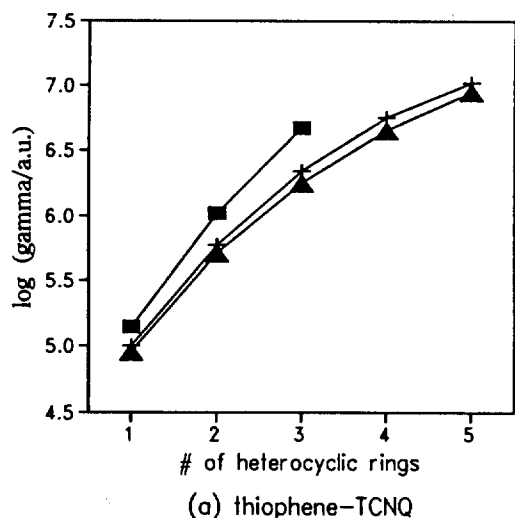
Figure 2. Plot of log scale of the third-order hyperpolarizabilities(γ) *versus* the number of heterocyclic rings(n) with respect to various frequencies, 0.00 eV (▲), 0.25 eV (1), and 0.50 eV (■).

(b) ~2.69 e7 and ~3.53 e7 a.u., selenophene-TCNQ(c) ~2.1 e7 and ~2.6 e7 a.u., respectively. Figure 2 shows that calcu-

lated values of the hetero-TCNQ(X=O, S, Se) systems all fit well to expression of the form:

$$\gamma = an^k \qquad (4)$$

In the case of polyenes, a number of theoretical studies have been devoted to power law dependences on the number (n) of monomer units with exponents(k) of ~4.0.[17-29] The n dependences of γ in Figure 2 shows that k values for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are thiophene-TCNQ(a) ~2.87, ~2.93, and ~3.17, furan-TCNQ(b) ~2.81, ~2.91, and ~3.22, selenophene-TCNQ(c) ~2.56, ~2.63, and ~2.88, respectively. In conclusion, the thiophene-TCNQ represents the largest α and γ values among the hetero-TCNQ (X=O, S, Se), whereas the furan-TCNQ represents the largest β values. The α and γ values decrease in the order: thiophene-TCNQ(a)>furan-TCNQ(b)>selenophene-TCNQ(c), whereas the β values decrease in the order: furan-TCNQ(b)>thiophene-TCNQ(a)>selenophene-TCNQ(c), as shown in Table 1. The magnitude of k of the thiophene-TCNQ are the largest among the hetero-TCNQ(X=O, S, Se).

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Synthesis, Properties and Structures of Discotic Liquid Crystalline Porphyrins

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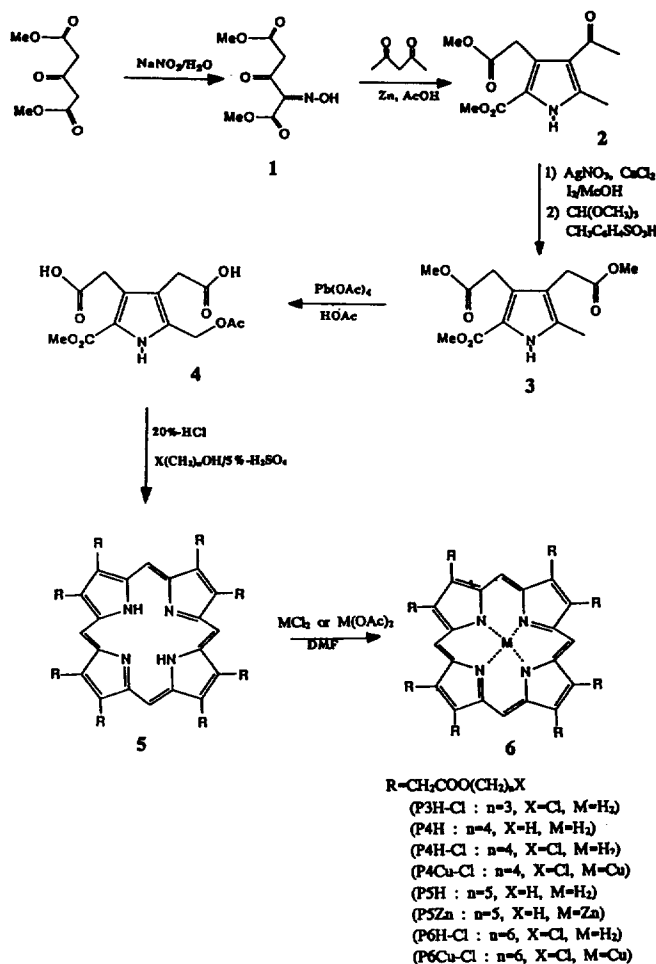[‡]*Insititute for Chemical Research, Kyoto University, Uji, Kyoto 600, Japan*
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R=CH₂COO(CH₂)ₙX
(P3H-Cl : n=3, X=Cl, M=H₂)
(P4H : n=4, X=H, M=H₂)
(P4H-Cl : n=4, X=Cl, M=H₂)
(P4Cu-Cl : n=4, X=Cl, M=Cu)
(P5H : n=5, X=H, M=H₂)
(P5Zn : n=5, X=H, M=Zn)
(P6H-Cl : n=6, X=Cl, M=H₂)
(P6Cu-Cl : n=6, X=Cl, M=Cu)

Scheme 1.

In recent years, discotic liquid crystals composed of flat rigid aromatic cores and flexible side chains have intensively been investigated for the applications as optical sensors, one-dimensional conductors, electrocatalysts etc.[1-5] We have synthesized several discotic liquid crystalline porphyrin derivatives having eight long alkylester chains. They contain two different central metals and eight side chains with various lengths of alkylgroups. This enables us to have the knowledge of transition temperatures from the crystalline phase to mesophase as well as structural changes between crystalline phase and mesophase.

Scheme 1 depicts the route to synthesize liquid crystalline porphyrin derivatives. By the reaction of β-ketoester with aq. sodium nitrite, dimethyl-1,3-acetonedicarboxylate oxime 1 was obtained. Methyl-3-acetyl-5-(methoxycarbonyl)-2-methylpyrrole-4-acetate 2 was prepared from 2,4-pentanedione and oxime derivative 1 in 49% yield by Knorr method for pyrrole synthesis.[6] After iodination of the acetyl terminal group of pyrrole 2, the resulting iodoacetyl pyrrole was reacted with trimethyl orthoformate/p-toluene sulfonic acid to get the dimethyl 5-(methoxycarbonyl)-2-methylpyrrole-3,4-diacetate 3 in 82% yield.[6] Continually, by the oxidation of compound 3 using lead tetracetate in acetic anhydride/acetic acid, dimethyl 5-(methoxycarbonyl)-2-(acetoxy methyl) pyrrole-3,4-diacetate 4 was obtained in nearly quantitative yield by a standard procedure.[7] Thereafter reactions were performed in one reactor without isolation of intermediates. In this reaction, the α-ester group of compound 4 was hydrolyzed firstly and then the ring-closure reaction for porphyrins was done using 5% sulfuric acid with alcohol.[8] In this step, alkyl ester groups with different chain lengths were introduced using appropriate alcohols. Finally the metalloporphyrins were obtained by refluxing the corresponding porphyrins using metal acetate or chloride in dimethylformamide.[9]

Reaction intermediates and final products were characterized by ¹H NMR spectroscopy. Obtained structures were matched with corresponding compounds. As representatives of this series, signals around −3.6 ppm and 10.3 ppm in ¹H NMR for metal-free butylester-attached porphyrin (P4H)[10] and chlorobutylester-attached porphyrin(P4H-Cl),[11] indicate -NH and meso-CH of aromatic porphyrins, respectively. The strong absorption peak, so called Soret band, at 405 nm in a UV spectrum of P4H which indicates porphyrin ring formation was also observed. When this porphyrin have no metal in the cavity, four weak absorption peaks appear at higher wavelength at 475, 523, 580 and 637 nm along with strong Soret band. However, in the case of metal complexation in the cavity, only two absorption peaks appeared. Such spectral features are already well known in porphyrin chemistry.[8,12] For other porphyrin derivatives similar spectral features were also observed.

The research on the resulting porphyrins focused on the possibility to control liquid crystalline transition temperature by insertion of different metals in the porphyrin cavity, and by substitution of heavy atoms in the side chain terminal as well as by attaching different side chain lengths. The answers to such objectives can be given in differential scanning