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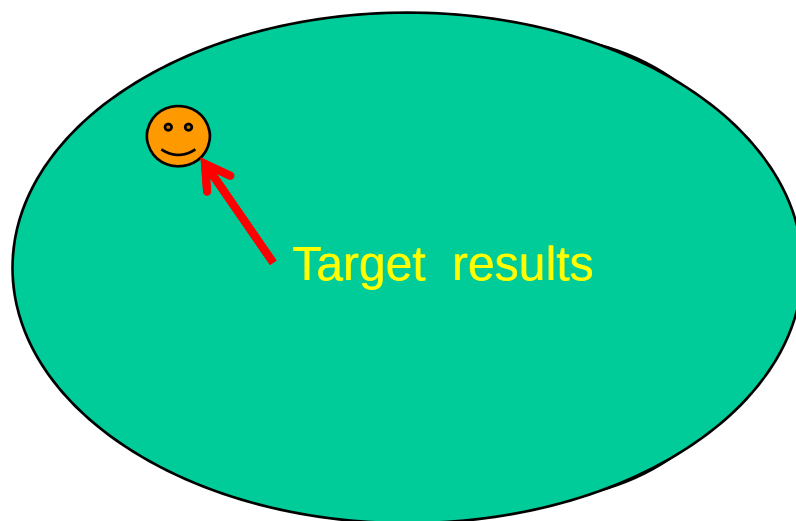
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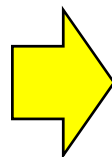
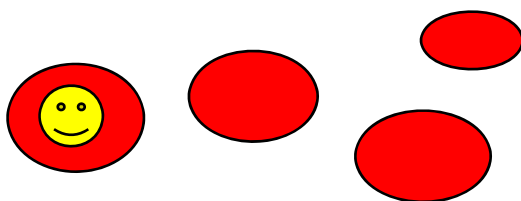
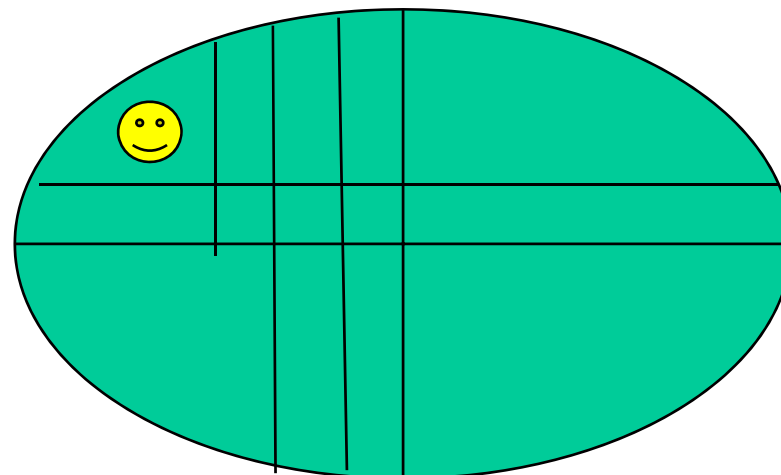
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領先

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可靠

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Fluorescence and Thermostability of Nanometer Porphyrin Trimer*

SHI Ying-yan^{1,2}, FA Huan-bao¹, ZHENG Wen-qí¹, LI Di¹, SHAN Ning¹ and WANG Xing-qiao^{1**}

1. College of Chemistry, Jilin University, Changchun 130023, P. R. China;

2. Department of Base Science, Jilin Institute of Architecture and Civil Engineering,

We cannot
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A nano-
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1002-9690(2006)01-014-03

Introduction

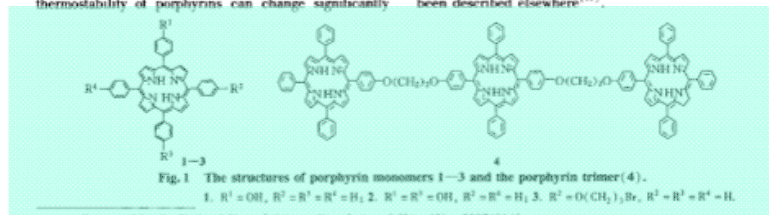
Porphyrin possesses some unique properties. In comparison with the porphyrin monomer, porphyrin oligomers are much attracting owing to their much better properties in some aspects, such as light harvest, energy transformation and electron transition. In recent years, oligomeric porphyrins with various structures have been under intensive research for their potential applications in molecular electronic and optic fields. For instance, multiporphyrin tapes or arrays may serve as molecular wires^[1-5], molecular switches^[6-8], photo funnels^[9], information storage^[10], and third-order nonlinear optical materials^[8]. In order to understand the effects of the peripheral substitution groups and oligomerization of porphyrin on the properties, we studied the UV-Vis and fluorescence spectra, and thermostability of the porphyrin trimer synthesized *via* a convenient route by using 1,3-dibromopropane as a bridge-linked agent. The results show that the fluorescence and the thermostability of porphyrins can change significantly

along with the change of porphyrin peripheral substitution groups as well as the oligomer formation. The kind of solvents and the symmetry of a molecular structure can also have very tremendous influence on the fluorescence and the thermostability of porphyrins. This investigation provides an available reference for the research on photosynthesis, molecular wires and logic gate circuits in molecular electronics.

Experimental

Pyrole (Fluka Chemika-Biochemika) and 1,3-dibromopropane (reagent grade) were freshly distilled prior to use. DMF and anhydrous K₂CO₃ were dried. Other chemicals were of reagent grade. The UV-Vis spectra were recorded on a Cintra 10 e UV-Visible spectrometer (GBC, Australia). The fluorescence spectra were obtained with a Perkin Elmer LS55 Fluorescence spectrometer. The TG/DTA curves were measured by a NETZSCH STA 449C analyzer.

The syntheses of all porphyrins (see Fig. 1) have been described elsewhere^[11].



* Supported by the National Natural Science Foundation of China (No. 20071014).

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Results and Discussion

1 UV-Vis Spectrum

The room temperature solution electronic absorption values are almost identical in Table 1. The characteristic absorptions of porphyrins are represented by the UV-Vis spectra of compounds 3 and 4 with a typical set of Soret bands and Q-bands in the visible region, which are similar to those of H₂MHTPP(1) and trans-

H₂DHDP(2). The band around 420 nm is assigned to the Soret band which arises from the transition of $a_{1u}(\pi) \rightarrow e_g^*(\pi)$, and the other four absorption maxima around 516, 550, 590 and 645 nm can be attributed to the Q-bands, corresponding to $a_{2u}(\pi) \rightarrow e_g^*(\pi)$ ^[12]. This indicates that porphyrin monomers being linked by —CH₂— have little effect on the electron delocalization of a π -conjugated porphyrin system.

Table 1. UV-Vis absorption spectra data of porphyrins 1–4 in CH₂Cl₂.

Compound	Soret band: $\lambda/\text{nm}(10^4\epsilon)$	Q-band: $\lambda/\text{nm}(10^4\epsilon)$	Q-band: $\lambda/\text{nm}(10^4\epsilon)$	Q-band: $\lambda/\text{nm}(10^4\epsilon)$	Q-band: $\lambda/\text{nm}(10^4\epsilon)$
1	418.40(0.3)	515.68(2.3)	547.68(1.8)	589.92(1.4)	645.52(1.2)
2	418.40(0.3)	515.68(1.0)	550.24(0.7)	589.92(0.4)	648.40(0.2)
3	418.40(0.4)	515.68(1.8)	552.80(1.3)	592.48(0.2)	648.80(0.6)
4	419.68(0.2)	518.24(0.1)	554.08(0.01)	593.76(0.3)	648.80(0.1)

2 Fluorescence Spectrum

Fig. 2 shows the fluorescence emission spectra of porphyrin monomers 1–3 and a porphyrin trimer. When porphyrins 1–4 were excited at 400 nm, the fluorescence emission peaks of porphyrins 1 and 2 lie around 471, 651 and 714 nm; the fluorescence emission peaks of porphyrins 3 and 4 are at 653 and 717 nm. The fluorescence emission peaks of porphyrins 1 and 2 at 471 nm can be assigned to the $S_2 \rightarrow S_0$ transition and it corresponds with the Soret band at 418.4 nm of their electronic absorption spectra^[13], but the fluorescence emission peaks of porphyrins 3 and 4 at the same position disappear. The fluorescence emission peaks at 650 and 714 nm of porphyrins 1–4 can be assigned to the $S_1 \rightarrow S_0$ transition and correspond with Q(0, 0), Q(0, 1) porphyrins 1–4^[14].

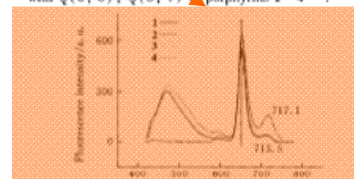


Fig. 2 The fluorescence emission spectra of porphyrin monomers 1–3 and a trimer (4) (excited at 400 nm).

The experimental results indicate that in dichloromethane, compared with those at 418 nm in the absorption spectrum, the fluorescence emission peak at 471 nm has several-nanometer displacement, which is caused by the lattice relaxation, that is, the electron has given its small part of energy to the crystal lattice by means of its interaction with crystal lattice in the form of heat, intensifying the thermal vibration of the

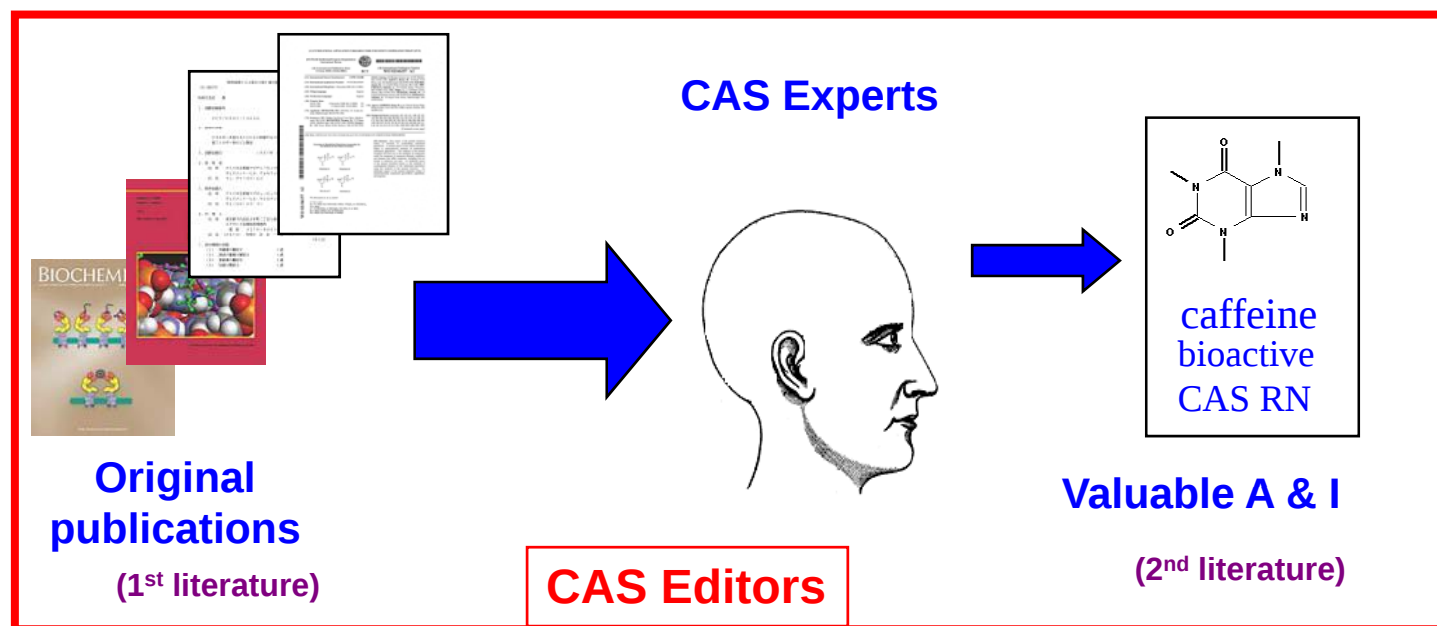
The main routes for the electrons in a conjugated system to transit from the excited states to the ground states are fluorescence radiation transition and nonradiation transition (interchange and system crossing). Compared with that of porphyrin 1, the fluorescence intensity of porphyrin 2 at 471 nm is stronger, for porphyrin 2 possesses two hydroxyphenyl groups at the *meso*-position, but porphyrin 1 has only one hydroxyphenyl group at the *meso*-position. Therefore, the different numbers of the porphyrin peripheral hydroxyphenyl groups result in the difference in the forms of energy releasing when electrons transit from a single excited state to the ground state. At 471 nm, along with the increase of porphyrin peripheral hydroxyphenyl groups, the non-radiation transition of electrons becomes weaker, while the fluorescence radiation transition becomes stronger. At the same position, the fluorescence emission peaks of porphyrins 3 and 4 nearly vanish because of the change of the porphyrin peripheral functional groups and polymerization. The non-radiation transition of electrons from the excited state to the ground state is the main form. This result shows that the porphyrin peripheral functional groups and polymerization have tremendous influence on the fluorescence property of porphyrins.

Fig. 3 shows the fluorescence excitation spectrum (monitored at 653 nm) and the emission spectrum of the trimer (excited at 400 or 327 nm) in CH₂Cl₂. The results in Fig. 3 confirm that different excitation wavelengths can only affect the fluorescence emission intensity, while they have no influence on peak position.

Fig. 4 shows the fluorescence excitation spectrum and the emission spectrum of the porphyrin trimer in different solvents, CH₂Cl₂ or DMF. It can be seen that the fluorescence intensity in DMF is stronger than that

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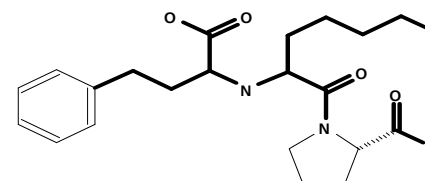
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Dr. Bruce Benjamin

analysis

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(51) International Patent Classification 7: C12N 15/31, C07K 14/81, C11D 3/33, 3/386		(11) International Publication Number: WO 00/01826	(43) International Publication Date: 13 January 2000 (13.01.00)
(21) International Application Number: PCT/US99/15246		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, EE, EG, ES, FI, FR, GB, GR, GU, HK, IL, IN, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, SM, SN, ST, SV, SZ, TD, TH, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (CH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, HE, IE, IT, LI, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 7 July 1999 (07.07.99)			
(30) Priority Data: 60/091,911 7 July 1998 (07.07.98) US			
(71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): SAUNDERS, Charles, Weston [US/US]; 3561 Carlsbad Court, Fairfield, OH 45014 (US); CORREA, Paul, Elliott [US/US]; 5755 Dry Ridge Road, Cincinnati, OH 45252 (US); SUN, Yiping [US/US]; 7589 Lakota Springs Drive, West Chester, OH			
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CAS RN 2835-34-8

Protein Sequence

1 MFPTIPLSRL FDNAMLRHR LHQLAFDTYQ EFEEAYIPKE QKYSFLQNPQ
51 TSLCFSESIA TPSNREETQQ KSNLELLRIS LLIQSWLEP VQFLRSVFAN
101 SLVYGASDSN VYDLLKDLLE GQTLMGRLD DGSPTGQIF KQYTSKFDTN
151 SHNDALLKN YGLLYCFRKM MDKVETFLRI VQCRSVEGSC GF

Somatotropin

Animal gene *pac43*

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CAS RN 154907-93-4

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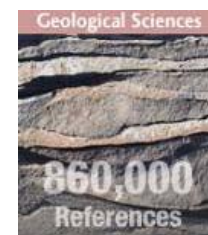
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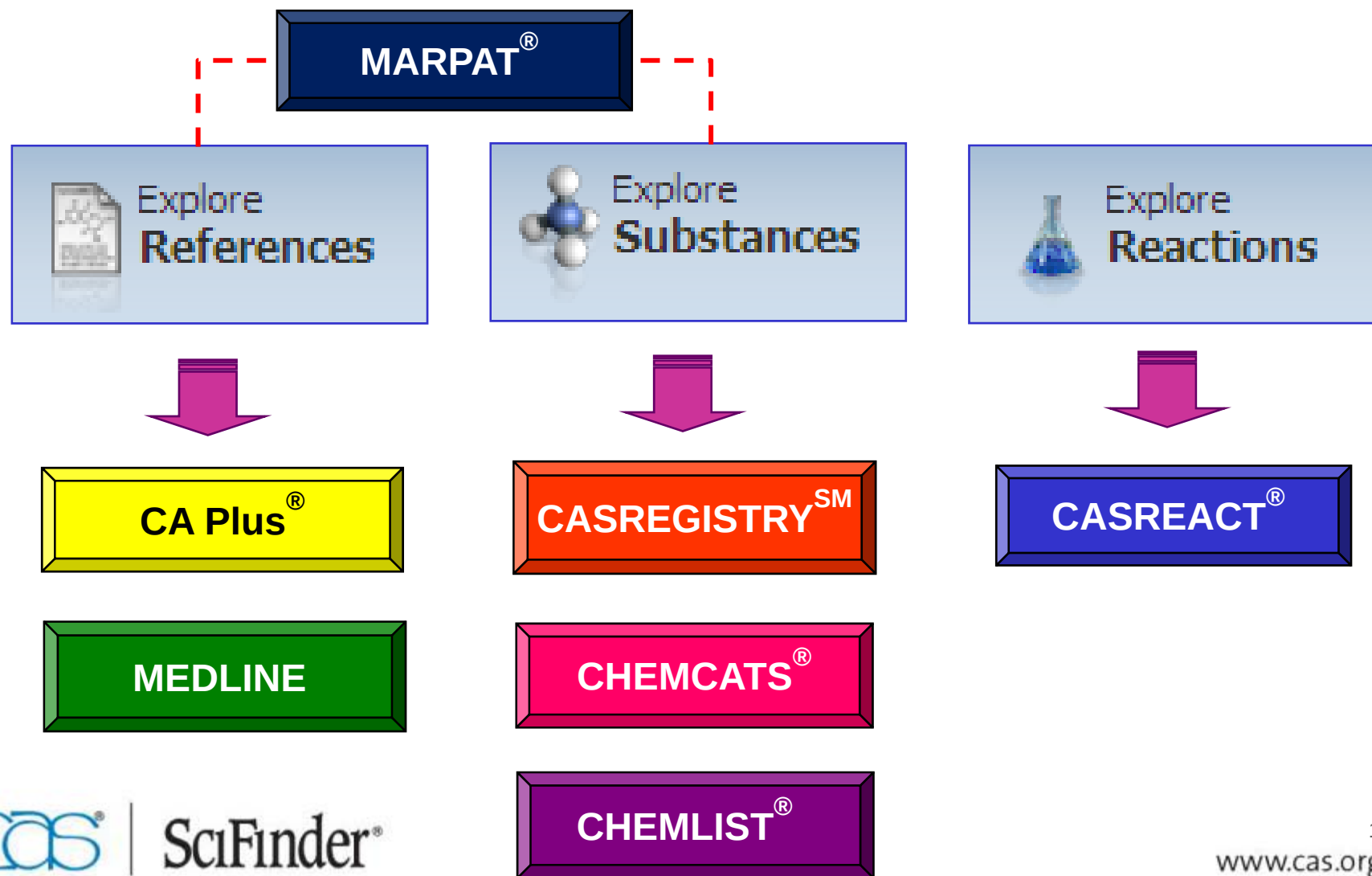
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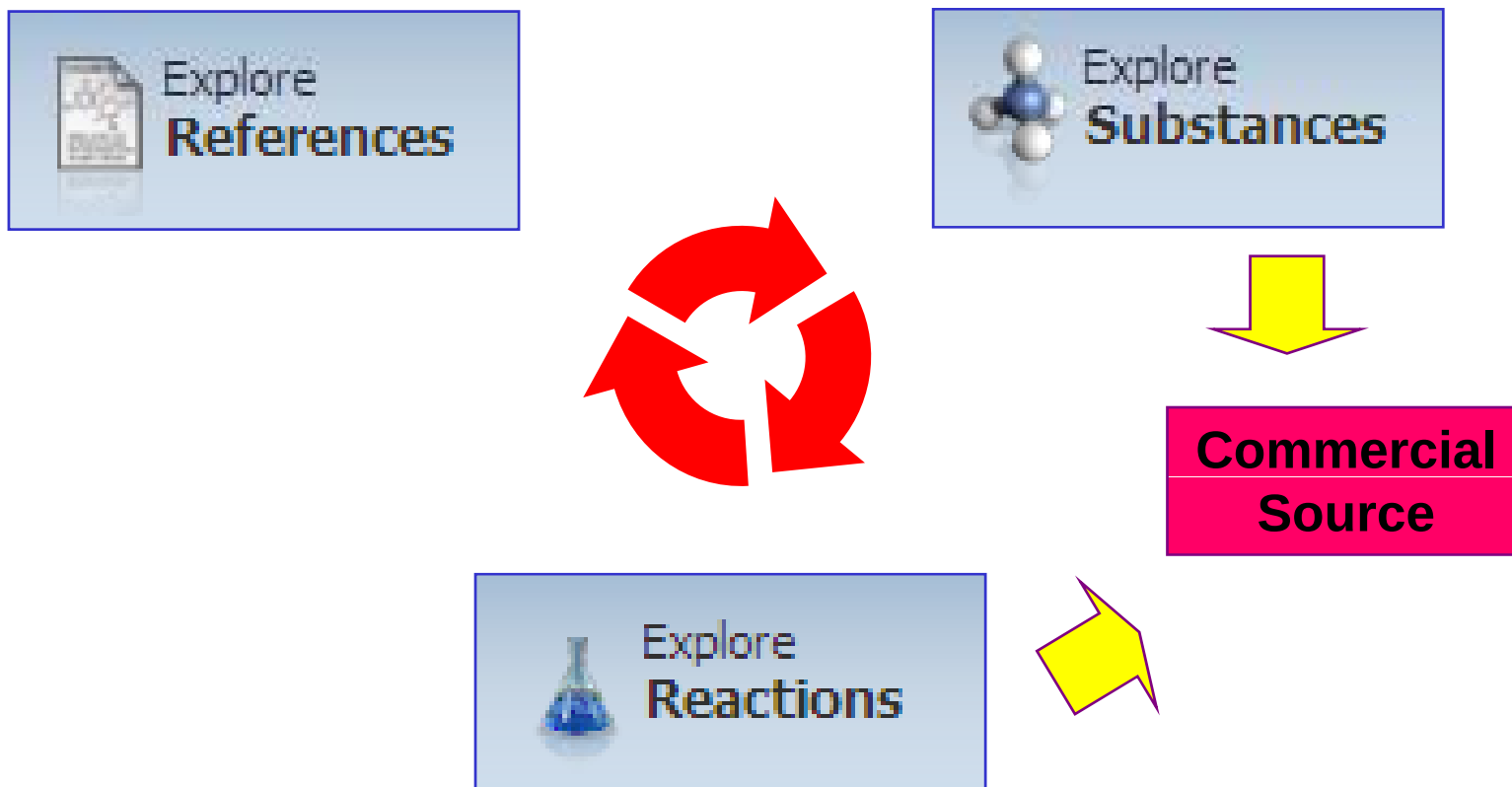
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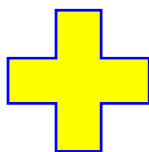
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