

(1) 可免費聆聽之線上演講

ACS Webinar: Rational Design of Safer Chemicals

<http://acswebinars.org/rational-design>

(2) Replacement of dichloromethane within chromatographic purification: a guide to alternative solvents

A total of 95 solvents were evaluated as potential replacements for CH_2Cl_2 as the bulk medium for chromatographic purification of a broad range of polar fragments and more complex molecules with functionality frequently encountered within Medicinal Chemistry programs. Based on this study, cyclopentyl methyl ether (CPME) would appear to offer considerable potential as a direct replacement for CH_2Cl_2 in binary eluents using MeOH as the modifier with MeOH–dimethyl carbonate (DMC) and i-PrOH–EtOAc also offering some potential advantages.

Green Chem. 2012, DOI: 10.1039/c2gc36378j

(3) Easily removable olefin metathesis catalysts

The homogeneous Hoveyda–Grubbs type catalysts containing a quaternary ammonium group can lead to organic products of high purity, which exhibit surprisingly low ruthenium contamination levels (usually below 5 ppm) after a simple and inexpensive purification step.

Green Chem. 2012, DOI: 10.1039/c2gc36015b



(4) Barriers to the Implementation of Green Chemistry in the United States

Via interviews with green chemistry leaders from industry, academia, nongovernmental institutions (NGOs), and government in the United States, six major categories of challenges commonly confronted by innovators were investigated: (1) economic and financial, (2) regulatory, (3) technical, (4) organizational, (5) cultural, and (6) definition and metrics. In particular, two elements of these that are particular to the implementation of green chemistry innovations are the absence of clear definitions and metrics for use by researchers and decision makers, as well as the interdisciplinary demands of these innovations on researchers and management. However, some of the strategies that have been successful thus far in overcoming these barriers, and the types of policies which could have positive impacts moving forward.

Environ. Sci. Technol., **2012**, *46*, 10892–10899.

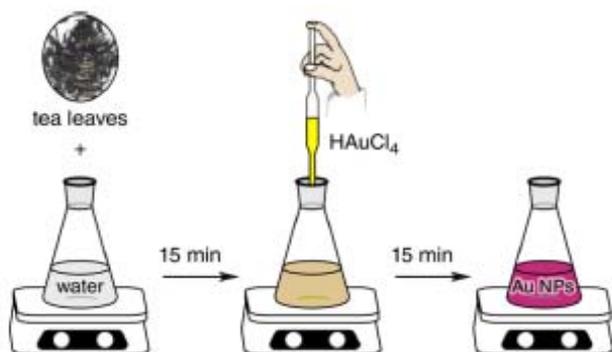


(5) Preparation of Gold Nanoparticles Using Tea: A Green Chemistry

Experiment (可以考慮列入大學普通化學實驗)

A simple, economic, and environmentally benign experimental route to synthesize gold nanoparticles using **tea leaves** in an aqueous media at room temperature is described with a goal to introduce chemistry students to the concept of green chemistry as well as nanotechnology. The single-step method circumvents the use of surfactant, capping agent, or template and follows several principles of green chemistry. The experiment can be conducted in a typical laboratory session and is suitable for incorporation into the undergraduate introductory chemistry laboratory curriculum and constitutes an influential example of green chemistry in action.

J. Chem. Educ. **2012**, *89*, 1316-1318.



(6) Green Chemistry Articles of Interest to the Pharmaceutical Industry in USA, including:

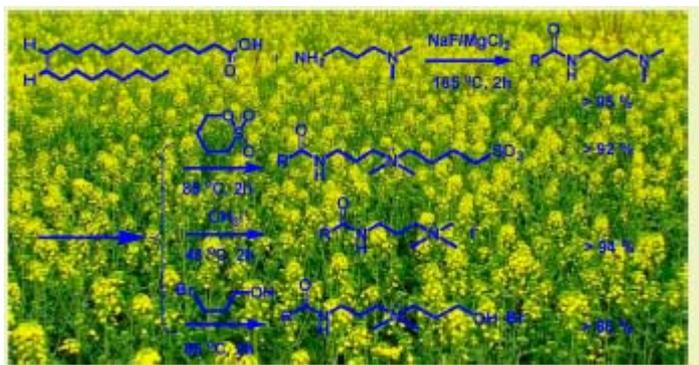
Green solvents, amide formation, oxidations, asymmetric hydrogenation, C-H activation, greener fluorination, biocatalysis, reductions, alcohol activation for nucleophilic displacement, chemistry in water, continuous processing and process intensification, and other general green chemistry consideration.

Org. Process Res. Dev. **2012**, DOI: 10.1021/op300251d

(7) Vegetable-Derived Long-Chain Surfactants Synthesized via a “Green” Route

A green route toward the preparation of vegetable-derived long-chain surfactants will be reported. The synthesis process possesses the following characteristics: bioresource-derived erucic acid (leftovers of rapeseed oil) was used as a starting material; no solvent was used and no chemical waste was produced; and high-yield products could be obtained in short reaction time. Compared with traditional surfactants bearing a saturated hydrophobic tail shorter than C18, the erucic acid-derived surfactants are more environmentally friendly because of their lower dosages in practical applications and the presence of the chemical degradable unsaturated bond and amido group in their molecular architecture.

ACS Sustainable Chem. Eng. 2012, DOI: 10.1021/sc300037e

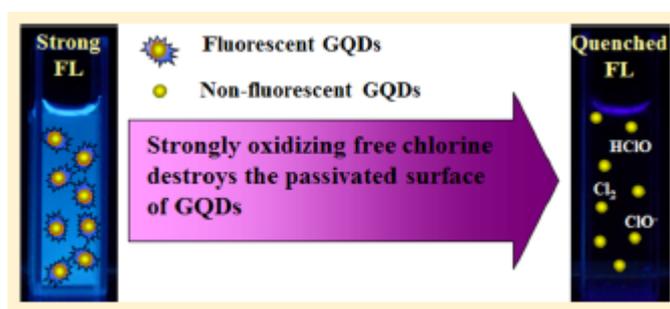


(8) Graphene Quantum Dot as a Green and Facile Sensor for Free Chlorine in Drinking Water

After optimizing some experimental conditions (including response time, concentration of graphene quantum dots (GQDs), and pH value of solution), a green and facile sensing system has been developed for the detection of free residual chlorine in water based on fluorescence (FL) quenching of GQDs. The sensing system exhibits many advantages, such as short response time, excellent selectivity, wide linear response range, and high sensitivity. The linear response range of

free chlorine ($R^2 = 0.992$) was from 0.05 to 10 μM . The detection limit ($S/N = 3$) was as low as 0.05 μM , which is much lower than that of the most widely used N-N-diethyl-p-phenylenediamine (DPD) colorimetric method. This sensing system was finally used to detect free residual chlorine in local tap water samples. The result agreed well with that by the DPD colorimetric method, suggesting the potential application of this new, green, sensitive, and facile sensing system in drinking water quality monitoring.

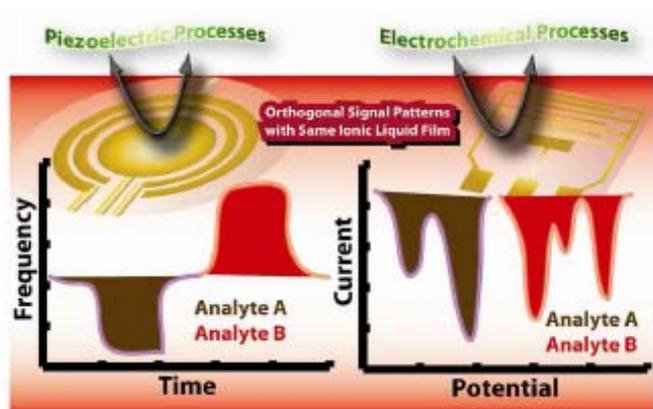
Anal. Chem., **2012**, *84*, 8378–8382.



(9) Ionic Liquids as Green Solvents and Electrolytes for Robust Chemical Sensor Development

Ionic liquids (ILs) exhibit complex behavior. Their simultaneous dual nature as solvents and electrolytes supports the existence of structurally tunable cations and anions, which could provide the basis of a novel sensing technology. Both piezoelectric and electrochemical formats through functionalized ionics that provide orthogonal chemo- and regioselectivity have been developed.

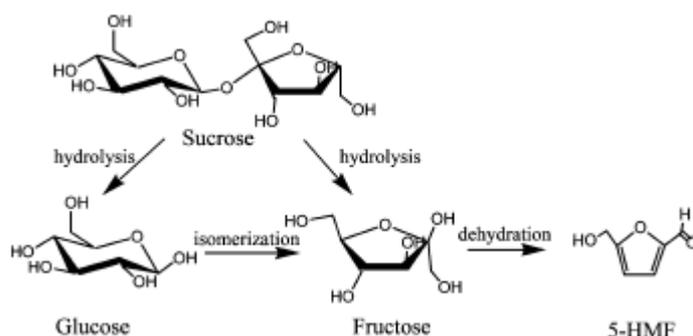
Acc. Chem. Res., **2012**, *45*, 1667–1677.



(10) Alkaline Ionic Liquids as Catalysts: A Novel and Green Process for the Dehydration of Carbohydrates To Give 5-Hydroxymethylfurfural

An efficient process for the conversion of carbohydrates into 5-hydroxymethylfurfural (5-HMF) catalyzed by the room temperature ionic liquid (IL) 1-butyl-3-methylimidazolium hydroxide ([BMIM]OH), using dimethyl sulfoxide (DMSO) as solvent, has been developed. The yield of 5-HMF obtained by hydrolysis of fructose at 160 °C with a mass ratio IL:fructose of 0.5 was 91.6%. The effects of varying the solvent, IL concentration, temperature, and reaction time on the reaction were studied in detail. The activation energy of fructose conversion was determined to be 99.2 kJ·mol⁻¹, with a pre-exponential factor of 2.1 × 10⁸. Furthermore, the catalyst also exhibited good activity for the dehydration of sucrose to 5-HMF under the same conditions.

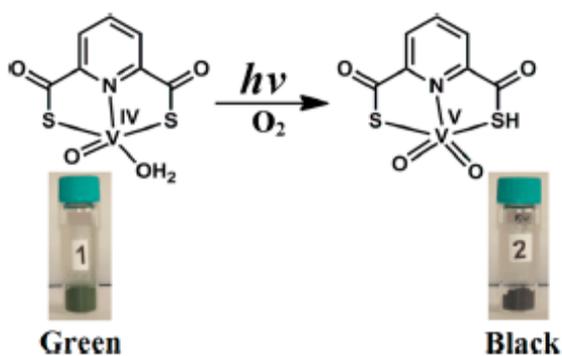
Ind. Eng. Chem. Res., **2012**, *51*, 13008–13013.



(11) Solid-to-Solid Oxidation of a Vanadium(IV) to a Vanadium(V) Compound: Chemistry of a Sulfur-Containing Siderophore

Visible light facilitates a solid-to-solid photochemical aerobic oxidation of a hunter-green microcrystalline oxidovanadium(IV) compound (1) to form a black powder of cis-dioxidovanadium(V) (2) at ambient temperature. This irreversible transformation of a metal monooxo to a metal dioxo complex in the solid state in the absence of solvent is unprecedented. It serves as a proof-of-concept reaction for green chemistry occurring in solid matrixes.

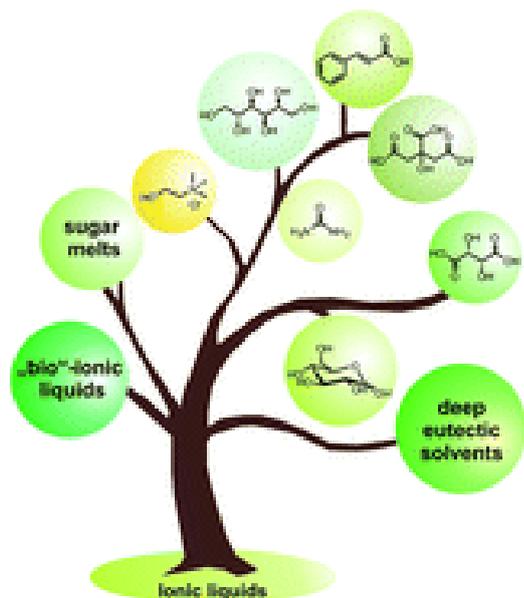
Inorg. Chem., **2012**, *51*, 9144-9146.



(12) Low melting mixtures in organic synthesis – an alternative to ionic liquids?

Deep eutectic solvents (DESs), defining as mixtures of hydrogen bond donor (HBD) systems with simple halide salts which produce liquids, are potentially better green solvents than ionic liquids (ILs), when HBDs are prepared from natural products. Some DESs have been employed as reaction media for organic synthesis and biotransformations.

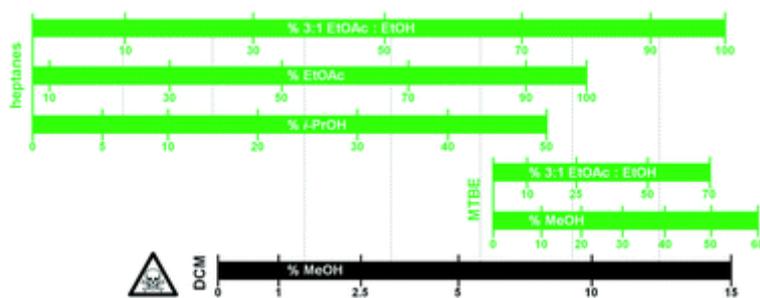
Green Chem., **2012**, DOI: [10.1039/c2gc36005e](https://doi.org/10.1039/c2gc36005e)



(13) A convenient guide to help select replacement solvents for dichloromethane in chromatography

An empirically-derived guide to aid synthetic chemists who wish to employ greener chromatography solvent alternatives to dichloromethane is presented.

Green Chem., 2012, DOI: 10. 1039/C2GC36064K



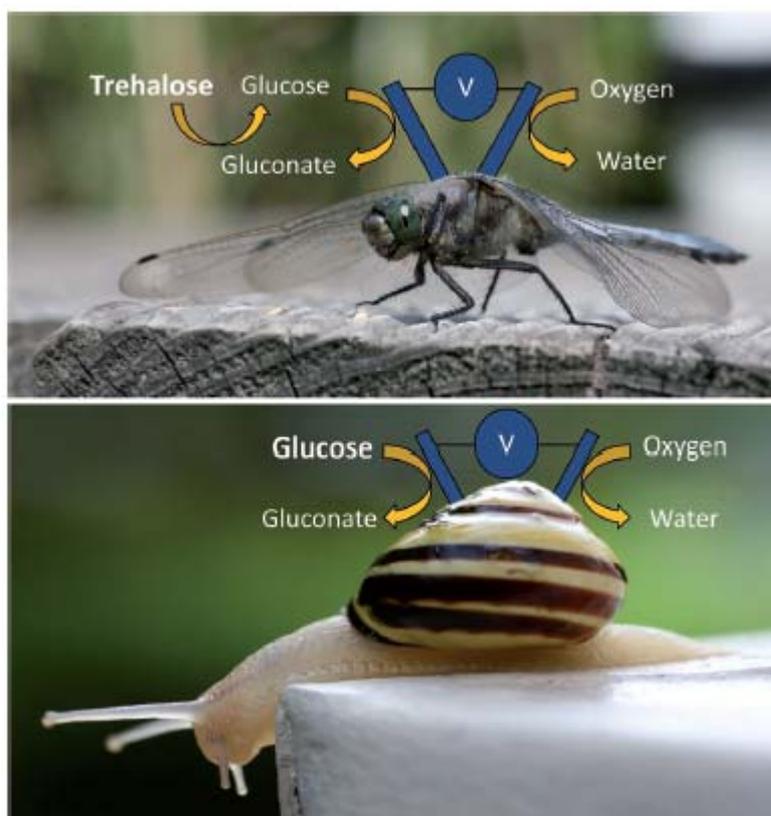
(14) 2012 European Sustainable Chemistry Award for Marc Taillefer and 2012 Presidential Green Chemistry Challenge Awards for Robert M. Waymouth, James L. Hedrick, Geoffrey W. Coates, and Yi Tang.

Angew. Chem. Int. Ed. 2012, 51, 9972-9973.

(15) From In Vitro to In Vivo—Biofuel Cells Are Maturing

Insects and molluscs as future biological drones for military purposes or environmental monitoring systems (see picture). Two research groups have demonstrated the successful implantation and operation of biofuel cells in snails, clams, and cockroaches. Owing to their simple circulatory systems, these invertebrates could be used in implantation studies without serious physical damage. These studies lay the cornerstone for the development of self-powered biomedical devices.

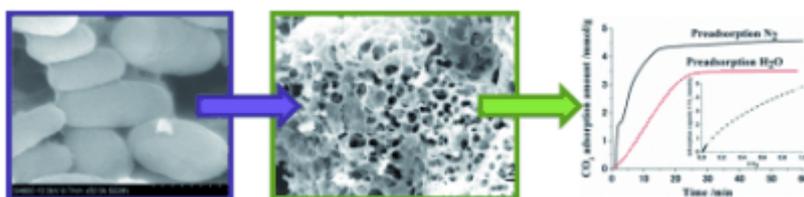
Angew. Chem. Int. Ed. **2012**, *51*, 9370-9372.



(16) Yeast-Based Microporous Carbon Materials for Carbon Dioxide Capture

Hierarchical microporous carbon materials prepared from yeast activated with KOH show excellent CO₂-capture capacity as a result of large numbers of nitrogen-containing groups and high surface area and pore volume. The amount of CO₂ adsorbed is higher, and the rate of adsorption is faster, than when directly carbonizing the same yeast.

ChemSusChem **2012**, *5*, 1274-1279.



(17) 化學合成效率度量法 (由中央研究院化學研究所甘魯生教授提供)

『度』和『量』在日常生活中無時無刻不在進行, 比如說我們對商品的第一個常有的反應是它的價格是否實在? 化學上酸鹼度 (pH) 值用來量度物質 (溶液) 是酸性或鹼性是公認之事, 這是因為 pH 值有公定的標準. 但是綠色化學是一朝向更簡單、更有效、更省能、更省時、更省成本等等比上一個過程更精簡的研究, 比呈現物質的酸鹼度要複雜得多. 因此度量的方法也是多面性. 不過減少化學反應的副產物 (廢物) 是首要之務. 因為副產物之產生代表了要用更多的原料, 要耗更多的能, 要需更多的時間將產物分離出, 要用更多的空間去處理. 也更能對環境及人體健康帶來衝擊. 本文對幾個化學反應效率重要度量方法簡介如下. 讀者可以據此小則可度量一化學反應是否值得繼續研究, 大則可度量 (化) 工廠所用之方法是否合乎綠色化學的要領.

產率(yield): 目標產物的當量和化學反應式平衡之後應得的產物當量之比。

$$\text{產率}(Y) = \text{產物之實當量(或重量)} / \text{由化學反應式計得之當量(或重量)}$$

原子經濟(atom economy): 產率值對化學反應之優劣可說是一目了然,但它卻沒說明目標產物在眾產物所佔之比.原子經濟之定義是目標產物中的原子在反應物所佔的份量。

$$\text{原子經濟}(AE) = \text{產物分子量} / \text{反應物分子量之和}$$

原子效率(atom efficiency): 是同時考慮了上二項的結合體。

$$\text{原子效率}(AF) = AE \times Y$$

有效質量產率(effective mass yield): 目標產物和所有反應物中有害物質之重量比.有害物質除了反應物及產物副產物外也包括所有參與的物質,如溶劑。

$$\text{有效質量產率}(EMY) = \text{產物的總量(公斤)} / \text{有害反應物的重量(公斤)}$$

碳原子效率(carbon efficiency): 無論是有機物或藥物.碳原子是結構的要素.所以針對碳原子有一個度量,即碳原子效率.它是產物中之碳原子量和所有反應物中碳原子量總和之比。

$$\text{碳原子效率}(CE) = \text{產物中碳原子總重量} / \text{反應物中碳原子總重量}$$

反應質量效率(reaction mass efficiency): 產物和留在溶液中的反應物重量之比。

$$\text{反應質量效率}(RME) = \text{產物重量} / \text{未反應之反應物總和}$$

(未完成反應物量等物反應物之總和 x 產率.)

環境因子(environmental factor): 反應後產物和反應中所有廢物之比.廢物包括了副產物及溶劑、催化劑、補助劑等。

$$\text{環境因子}(E) = \text{廢物的總量(公斤)} / \text{產物的重量(公斤)}$$

每一種度量法的產生都有它的背景, 比如說產率 Y 常出現於有關之學術論文中. 因為在實驗室中產率之高低是反應之取捨的首要指標. AE 和 AF 則考慮到就算 Y 值高, 若目標產物在眾(副)產物佔之份甚少, 是否有經濟價值? EMY 將反應中的溶劑及其他之輔助劑列入計算. CE 由美國藥廠 GlaxoSmithKline 提出, 此法常用在藥物合成反應上. RME 和 E 都是以整個製造過程所有的廢物列入計算. 是估算工業製程綠不綠的重要指標.

想一想: 請指出以上各指標中數值大或小者的化學反應效率為高.

(18) 碳足跡 (由中央研究院化學研究所甘魯生教授提供)

碳足跡這名詞是由 carbon footprint 直譯而來. 它的定義由直接和間接支持人類的活動所產生溫室氣體的總和. 愈來愈多的証據顯示溫室氣體是造成氣溫上昇及氣候異常的元兇. 常見的溫室氣體有二氧化碳、甲烷及臭氧. 因人類活動產生二氧化碳遠比其它溫室氣體多得多. 所以碳足跡就是產生二氧化碳的度量法. 可依個人、家庭、社區、國家以及機器、生產線、工廠等為單位每年所產生之二氧化碳(噸)來計算. 比如說下列之事項都能產生一公斤二氧化碳:

生產 5 個塑膠袋. (註一)

生產 2 只塑膠瓶.

操作電腦 32 小時(功率 60 瓦計).

開車 6 公里.

乘公共交通工具 12 公里.

乘飛機 2.2 公里.

吃 1/3 個乳酪漢堡. (也就是說製一個乳酪漢堡會產生三公斤二氧化碳!)

我們日常生活離不了用電, 發電產生之二氧化碳量要看所用之燃料而定.

化石燃料

以煤發電平均 1.1 度 (1 kWh)

以天然氣發電 2.0 度

以石油發電平均 1.3 度(註二)

再生燃料

水力發電 250 度

日光能發電 6.7 至 16.7 度

風能發電 45.5 至 333 度

木材或其他之生物質發電 0.67 度

核能

核能發電 167 度(註三)

看了以上之統計數字之後若要減少釋放二氧化碳到大氣中的方法是少用塑膠袋、多乘公共交通工具、少吃加工之食品及少用電等,也就是個人的生活中要時時考慮到碳足跡,要在習慣上有所修正.在發電方面則要多用再生能源如日光能、風能、及水力,比較安全的燃料(相對於核電).

註一：以每公升汽油產生 2.3 公斤及每公升柴油產生 2.7 公斤二氧化碳計算.

註二：US Energy Information Administration

<http://www.eia.gov/tools/faqs/faq.cfm?id=74&t=11>

註三：Yahoo Answers

<http://answers.yahoo.com/question/index?qid=20070930191518AA7yWqo>