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Organic Electronics and Photonics: Concluding Remarks

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Summing up the scientific content of a Faraday Discussion Meeting in a short paper is an impossible task and therefore, I have tried simply to draw-out a few more-general themes relating to the presentations made and the exciting research field that encompasses them. These are personal observations and should not be considered either comprehensive or 10 impartial.

It is in fact rather difficult to find a singular descriptor for the research field considered at Faraday Discussion Meeting 174; the label *organic* electronics and photonics is something of a misnomer since the devices fabricated generally also contain both metals 15 and metal oxides and can contain inorganic molecules as well as organic ones. But equally, *Molecular* electronics is incomplete, ditto for *printed* electronics; the materials used are not all molecular or necessarily printable. Should we simply say electronics and photonics and forget about the adjective? That would, I fear, be too general as there are many aspects of electronics that we do not (and cannot) address like central processing 20 units (CPUs), graphical user interfaces (GUIs) and other components that require processing and data capacities far beyond our reach. *Large area* electronics is another possibility since this tends to rule out wafer-based materials. My own preference, however, is for *plastic* electronics and at Imperial College we have named our collective activities across physics, chemistry and materials science, the Centre for Plastic 25 Electronics. It is so called because that adjective reflects, at least to us, a very practical combination of easy processing and functional properties and it is this same duality that has motivated and continues to motivate much of our interest, certainly in respect of applications, in solution processed semiconductors. Plastic also has the connotation, in biomedical science, of reconfigurable and that chimes with our general outlook as well. 30 Plastics are moreover, in popular culture, often considered 'cheap and cheerful' and jolly useful; attributes we would surely wish for organic electronics and photonics as well.

The molecular nature of plastics means that they typically have strong bonding along the chain (*intra*-molecular) but relatively weak bonding between neighbouring chains (*inter*- 35 molecular): The inter-molecular, characteristically van der Waals, bonds are roughly a twentieth as strong. This helps processing since the chains can be relatively easily separated, via heat (melt-processing) or a solvent (solution-processing), and then reassembled into new shapes, for instance conforming to the elaborate features of a mould or to a curved surface to thereby produce kitchen goods, drinks bottles or 40 packaging bearing branding and labelling information. The same van der Waals solid or 'soft solid' properties apply to the solution processing of polymer and other (small molecule) organic and organo-metallic semiconductors, conductors and insulators that are widely used in our field. They are, moreover, at the centre of most that is of particular interest in respect to the optical and electrical properties of this class of materials. What's 45 more they underpin the processing and some of the properties of colloidal metal and inorganic semiconductor particles, nanotubes and 2-D materials including the transition metal dichalcogenides and related systems. In the end the plastic electronics tag can reasonably encompass all of these materials types especially if used in a way that helps us along the path to solution-based, low-temperature, high-throughput and (ideally) low- 50 capital-cost fabrication of displays, lighting, solar cells, photodetectors, electronic circuits and photonic components.
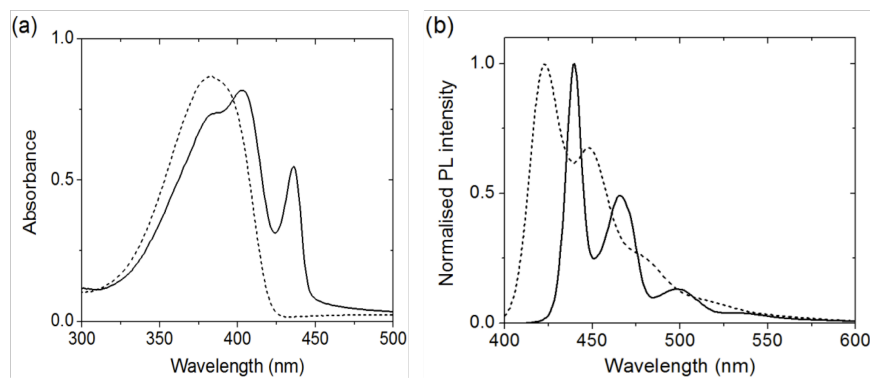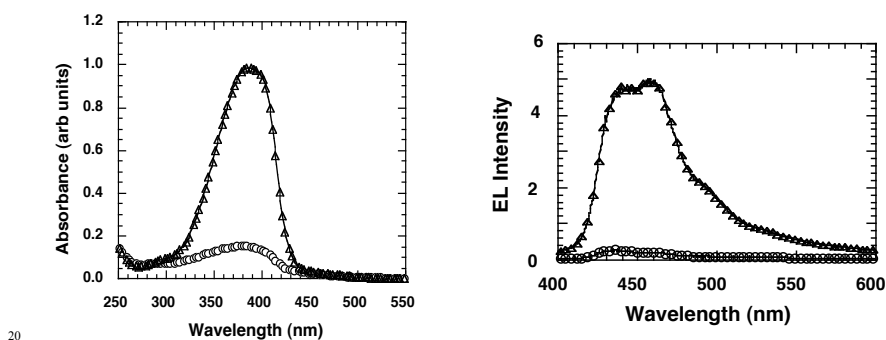
Figure 1. (a) Absorbance and (b) Photoluminescence (PL) spectra of a hot spin-coated (toluene, 100 °C), 100 nm thickness PFO glassy film before (dashed line) and after (solid line) flooding the film surface with decalin to generate a high fraction of β-phase chain segments. The β-phase PL vibronic structure is particularly well-resolved and characteristic of a rigid, chain-extended, planar structure. The absorbance spectrum for the decalin-immersed sample comprises contributions from both β-phase and glassy (α-phase) chain segments whilst the PL spectrum is dominated by β-phase segment contributions, populated via both direct excitation and following rapid energy transfer from the α-phase. (unpublished data, courtesy of Alexandr Perevedentsev).

Another reason to mention plastic electronics, perhaps, is that, as noted by Professor Fred Wudl in his introductory lecture, it is now twenty-five years since the 1989 demonstration of conjugated polymer electroluminescence from precursor-route poly(*p*-phenylenevinylene) diode structures. The associated 1989 patent[1] led to the 1992 founding of Cambridge Display Technology (now part of the Sumitomo Chemical Company) and the 1990 *Nature* paper[2] that followed has become one of the most highly cited articles in the physical sciences. This work can in many ways be considered the start of plastic electronics, acting as a trigger point for an explosion of interest in solution-processed semiconductors within both industrial labs and academic/government institutions. Its publication came at a critical juncture when interest in conjugated polymers was otherwise starting to wane following (i) their failure to live up to the expectations derived from the label "synthetic metals" and (ii) their inability to deliver the large, ultrafast non-resonant nonlinearities sought for all-optical switching.[3] The new directions opened by this paper transformed the field and it has gone from strength to strength with organic semiconductors now being considered mainstream. Ten years later, the significance of polymer-based synthetic metals was recognised by the 2000 Nobel Prize for Chemistry, awarded to Professors Heeger, MacDiarmid and Shirakawa.[4]

Professor Wudl focused his introductory talk on low band gap conjugated polymers and doping effects, reprising the development of charge transfer salts, the sulphur nitride polymer SN_x, poly(isothianapthene) (PITN) and related materials and discussing the development of new strong electron acceptor moities such as benzobisthiadiazole (BBT) and their donor-acceptor copolymers with diketopyrrolopyrrole (DPP).[5] Professor Wudl also commented that (small) molecules are increasingly being used in preference to polymers because it is easier to control (limit) their structural polymorphs in order to obtain more reproducible thin film properties – essential for any commercialisation. This is certainly a direction of travel, with both solution processed and vacuum sublimed deposition protocols, but there are examples of polymers that have very precise and reproducible structures. I have a strong interest in poly(9,9-dioctylfluorene) (see Figure 1) for which the β-phase chain segment conformation is especially well defined.[6]

Figure 2. Polarised absorption (left) and electroluminescence (right) emission spectra (triangles – parallel polarised, circles – perpendicular polarised) for poly(9,9-dioctylfluorene) homogeneously aligned in the nematic liquid crystal phase on a rubbed precursor-route poly(*p*-phenylenevinylene) (PPV) alignment layer. The absorption anisotropy is limited (≤ 7) by the liquid crystal order parameter and the π-π* transition dipole moment orientation relative to the chain axis projection. The higher (≤ 25) EL anisotropy is consistent with an emission zone localized close to the PPV alignment layer interface where the order parameter is enhanced relative to the bulk that is measured in absorption.

The patterning of β-phase chain segments via a simple dip-pen nanolithography procedure then offers a novel approach to the fabrication of nanophotonic structures.[7] Generation of the β-phase yields a conformational metamaterial; the sub-wavelength physical structuring strongly alters the material's interaction with electromagnetic radiation. Such avenues of exploration might be thought of as being analogous to the "silicon-approach" to semiconductor device fabrication in which desired properties are generated by processing (oxidizing, doping, etching) an otherwise uninteresting (from a semiconductor device perspective) intrinsic Si wafer. Much more also needs to be learned, in general, about how to tune weak interactions to thereby select specific molecular architectures and packing motifs. Professor Perepichka described, for instance, the use of complementary H-bonding in the formation of p-n heterojunction structures comprising p-type dipyrrolopyridines and n-type napthalenediimides.[8]

As already noted above, the molecular nature of many of our materials defines their functional properties. Wavefunctions localised to molecular units lead to large oscillator strengths (absorption coefficients ~ 10^5 cm^{-1}), coupling between electronic and vibrational degrees of freedom (polaronic charge states and vibronic structure in absorption and emission spectra – see Figure 1), a distinct manifold of triplet states and, in combination with a low dielectric constant, to strongly bound excitons. These in turn typically lead to radiative decay times ~ 1ns, to 1/e absorption depths ~ 100 nm that allow thin film structures to efficiently absorb solar energy, to broad emission bandwidths that can support short pulse optical gain, to hopping transport and to selection-rule-limited electroluminescence quantum efficiency. Nanometric length scales are also important e.g. Kuhn segment lengths for conjugated polymers ~ 10-30 nm, exciton diffusion lengths ~ 5-50 nm, and Förster transfer radii ~ 1-10 nm but that is more a happenstance of the fact that we are dealing with molecular materials; nanometers are the natural length scale for molecules. Molecular orientation also matters (See Figure 2)[9]; it exposes the intrinsic anisotropy of many physical processes and can significantly affect the observed charge transport and light absorption and emission properties. State of order (glass/crystal/liquid crystal; mono-/poly-domain) has also been used to good effect in

establishing and understanding trade-offs between processing protocols and ultimate properties, especially for blends. An interesting example is the effect that solution pre-ordering has on the optical properties of poly(*p*-phenylenevinylene) thin films.[10]

5 The properties of individual molecules (in terms of geometry and electronic structure) are readily perturbed by the environment in which they sit; the 'usefulness' of a molecular material then often depends on the details of its processing and the form in which it is used. Six presentations (Solomon *et al*, Baldea *et al*, Venkatramani *et al*, Venkataraman *et al*, Xu *et al* and Ottosson *et al*) at the Faraday discussion meeting addressed single- or 10 few-molecule electronics, from both an experimental and a theoretical perspective, a topic that presents serious challenges for measurement and understanding but that can, for instance, offer important perspectives on the question: For how long will Moore's law continue to be obeyed? Exacting sample fabrication and measurement make this topic one for the specialist but it should also have a much broader significance in helping to 15 understand the function of self-assembled monolayers and other ultrathin interlayer materials in modifying the injection properties of electrodes.[11, 12] Many of the other presentations at the meeting considered more conventional electronics and photonics based on samples that are essentially macroscopic within the film-plane but nevertheless equally reliant on molecular properties and controlled by local environments.

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One good example of the influence of environment is the class of molecules used as laser dyes that have close to unity quantum yield in dilute solution but whose fluorescence is drastically reduced in powder form by so-called concentration quenching. The use of low concentrations of laser dye 4-(Dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-25 4*H*-pyran (DCM) dispersed in a *tris*(8-hydroxyquinolinato)aluminium (Alq_3) host as an optical gain medium in the research reported by Professor Lemmer and Dr Brückner represents the solid state equivalent; the Alq_3 host material keeps the DCM laser dye molecules far enough apart that they function as if in dilute solution. In Professor Lemmer's case the interest was in distributed feedback (DFB) lasers for use as light 30 sources in lab-on-a-chip-based microfluidic analysis. Other approaches to the instrumentation of such structures include the use of OLED light sources and organic photodetectors.[13, 14] The narrow laser linewidth in Professor Lemmer's devices, without the characteristic longer-wavelength vibronic tail found for most OLEDs, is beneficial to avoid overlap between excitation light and analyte fluorescence in biomedical assays.[15] 35 In Dr Brückner's structures the organic gain medium was interacting with a metal-containing vertical distributed-Bragg-reflector-encased photon environment that sustained Tamm plasmon polaritons. Related DBR-controlled photon environments include microcavities used to study strongly- and ultrastrongly-coupled exciton-photon mixed states (polaritons). A second example, not, however, discussed extensively at the 40 meeting, is the pentacene doped p-terphenyl crystal that recently allowed fabrication of the first room temperature Maser[16] via optically pumped population inversion amongst the triplet sublevels of pentacene. In both of these cases, dilution prevents unwanted inter-molecular interactions and allows the properties of the individual molecule to shine through. Interestingly, films of many conjugated polymers do not greatly suffer from 45 such concentration quenching effects (see Figure 3),[17] although some do.[18]

H- and J-aggregates,[19] excimers and exciplexes also depend for their formation on intermolecular interactions, with interactions in the excited state key for the latter two. J-aggregated cyanine dyes have an enhanced absorption strength (and suppressed vibronic 50 coupling) that was used for many years to good effect in sensitizing silver halide based photographic emulsions. More recently this large oscillator strength was shown to allow the fabrication of strongly coupled DBR-based microcavities that emit from hybrid exciton-polariton states.[20] The observed room temperature Rabi splittings are very substantial for this and a range of other molecular materials.
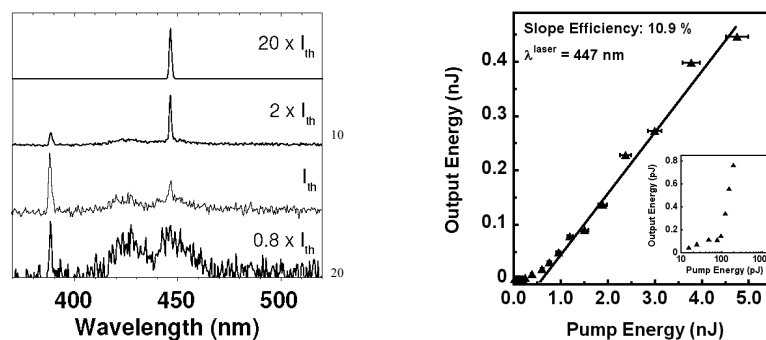
Figure 3. Laser spectra (left) and input-output characteristics (right) for a 447 nm one-dimensional DFB laser comprising a 90 nm thickness film of poly((9,9-dioctylfluorene)$_{0.8}$-co-(9,9-di(2-methyl)butylfluorene)$_{0.2}$) (Y80F8:20F5) spin coated on top of an etched silica grating (period Λ = 290 nm, 75% fill factor). The laser was pumped with 10 ns, 10Hz laser pulses at λ_{ext} = 390 nm. The lasing threshold, $I_{th} \approx$ 100 pJ (see inset to right panel) corresponds to 0.3 mJ/cm^2 and combined with the measured slope efficiency of ~ 11% represents state-of-the-art performance for a conjugated polymer laser.

Intermolecular interactions are likewise key for charge transport through the bulk of a film which requires charges to transfer between neighbouring units, even when long chain polymers are used.[17] This can be strongly affected by the state-of-order and inter-molecular packing as discussed by Professor Nelson and Dr McDouall. Crystallinity is not a pre-requisite with some of the highest mobilities in polymers arising for non-crystalline materials.[17] Charge trap states tailing into the optical gap can strongly affect the overall carrier mobility and its temperature dependence. In many cases an exponential gap state distribution provides a good model to explain a variety of experimental observations.[21]

Chemistry allows the tuning of many molecular properties including highest occupied and lowest unoccupied molecular orbitals (HOMOs and LUMOs) whose energy difference determines optical gap and thence absorption and emission spectra. Ionization potential and electron affinity, thermal properties e.g. glass and isotropic melt transition temperatures and the existence of any liquid crystal phases, solubility and the tendency to pack in, for example, herring-bone or cofacial stack arrangements are also controllable through the chemical structure design of both the conjugated core and peripheral solubilising groups. Not all synthesis routes are, however, equivalent and for example the difference between the Wittig and Gilch syntheses of dialkoxy-*p*-phenylenevinylene polymers had an enormous impact on progress in OLED device performance with Gilch-route polymers[22] substantially outperforming on-paper-similar Wittig-synthesised materials.[23] Likewise, for fluorene-based polymers the Suzuki route proved especially useful[24] and current state of the art fluorene-based complex copolymers are Suzuki-coupled.

Differences in defect type and density, often at the detection limits of standard chemical analyses can have a major influence on device performance. Moreover, different device types and measurements may be more or less susceptible, for example the high carrier densities in transistors allow for significant trap filling that does not happen in time-of-flight photocurrent measurements performed at much lower densities.
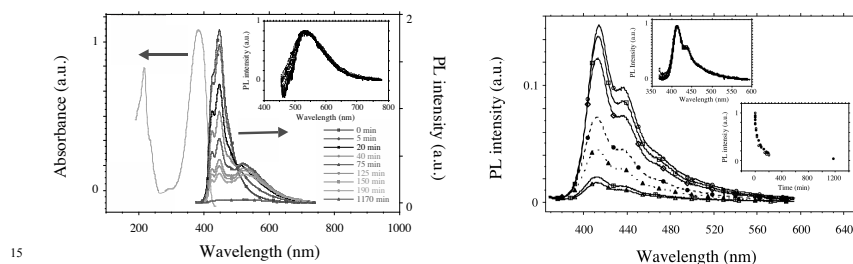
Figure 4. Influence of local environment on the PL emission spectral changes induced by photo-oxidation of PFO thin films by exposure to UV radiation in air. Left panel shows the PFO absorbance (left ordinate) before irradiation and a sequence of PL spectra (right ordinate) recorded over time during irradiation. The inset shows the normalised green-band excimer emission spectra extracted from each of the irradiated sample spectra by subtraction of a scaled pre-irradiation PFO PL spectrum. Right panel shows the equivalent experiment performed for a PFO sample dispersed at low concentration in a polystyrene matrix film that prevents excimer formation. No green-band emission is observed; the PFO spectrum simply decreases in magnitude (see upper inset for peak normalised data). The lower inset shows the temporal decay of the integrated PL for this sample and superimposed data for the green-band-subtracted blue emission component of an undiluted film irradiated under the same conditions.

Defect concentrations of a few percent, that might simply be what is present at the chain ends of a moderate molecular weight polymer, would be considered high in conventional semiconductor terms. Add to this the potential for catalyst residues, ionic impurities leached from the glassware, simultaneous synthesis of isomeric compounds, non-uniform coupling reactions, differing regio-regularities and oxidative products formed during storage and processing and it is small wonder that there can be a spread in reported performance for nominally the same materials. The influence of defects can also depend on environment, for instance the fluorenone oxidative degradation products in poly(9,9-dialkylfluorene) polymers only modify the emission spectrum when they are able to form excimers that are then responsible for the characteristic green-band emission; if the polymer chains are isolated in a matrix then the only effect is a decrease in overall PL efficiency due to the quenching properties of the fluorenone moiety (see Figure 4).[25] It should thus be evident that developing 'good' synthesis routes, effective procedures for impurity control and material-safe processing methods are necessary pre-requisites to undertaking true structure-property relationship studies.

Added complexities may occur when one looks to develop hybrid/composite materials such as the novel II-VI inorganic semiconductor/conjugated polymer systems discussed by Dr Kim for use in solar energy generation. Here the favoured (for charge generation and collection) bulk heterojunction geometry is being formed *in situ* by chemical synthesis of the II-VI colloidal particles within the polymer matrix. The potential benefits of such hybrid systems can, however, be great as for example the newly developed use of methylammonium lead iodide and related perovskites for solar cells has demonstrated.[26] Hybrids can also encompass photonic structures, for instance those that dipole-dipole couple (In,Ga)N quantum well Mott-Wannier excitons with polyfluorene Frenkel excitons and that lead to efficient non-radiative energy transfer between the two.[27]

Professor Sasaki described a different composite system, in his case for photorefractive data storage, comprising mixtures of several ferroelectric LCs and 2,4,7-trinitrofluorenone (TNF) as an oxidative dopant. Photorefractive composites comprise a

field in which one of this year's Nobel Laureates in Chemistry, W.E. Moerner, made seminal contributions at IBM.[28] Photorefraction is also found in conjugated polymers but it and other nonlinear optical effects are little studied at present.[29] W.E. Moerner shared the 2014 Nobel Prize for his work on super-resolution fluorescence microscopy, a technique that might in the future be usefully applied to organic electronic and photonic materials systems to better understand their film microstructure.

Biomedical applications represent another interesting arena for the application of organic electronic and photonic devices as already mentioned above in connection with Professor Lemmer's presentation. This arena is sometimes referred to as Bioelectronics and is seen as a promising outlet for the application of organic electronic and photonic devices.[30] In addition, within this meeting Dr Fabroni described work on organic single crystal X-ray detectors, Professor Torsi on ZnO transistors, Dr Melzer on electrolyte gated transistors, Dr Laurand on truxene-based DFB lasers and Dr Dennany on solution phase electrochemiluminescence; all for use in imaging or sensing applications.

Dr Zysman-Colman also discussed electrochemiluminescence but in his case, the context was for use in light emitting structures for displays, more specifically focused on achieving efficient blue-light emission. This of course is the topic that has been recognized by the 2014 Nobel Prize for Physics, awarded to Professors Akasaki, Amano and Nakamura for their invention of the GaN-based blue LED that has produced a breakthrough in high efficiency solid-state lighting.

For those of us working in the organic LED (or OLED) field, it is perhaps fortunate that GaN LEDs were unknown at the time of the invention of OLEDs based on (i) vacuum sublimed small molecules, including Alq_3, by Tang and van Slyke at Kodak Research Labs in Rochester[31] and (ii) solution processed conjugated polymers (by Burroughes, Bradley and Friend[2] at the Cavendish Laboratory, Cambridge). Otherwise, this technology would surely have been harder to establish. It has taken twenty-five years but we have now seen OLEDs commercialized for use in mobile phone, tablet and television displays (a sector in which GaN LEDs are used to backlight liquid crystal displays) and they are starting to enter the lighting arena in direct competition to GaN-based LEDs. OLEDs can be fabricated as large area emitters whilst GaN LEDs are point source emitters and that difference in form factor will likely influence how they are used.

It is interesting finally to reflect on how many times statements that have acquired *accepted wisdom* status turn out to be incorrect. Good advice to someone entering a research field would be to beware such strongly held statements of belief. For example, in my own research career I have been told '*It is well known that…*

    ….. polymer semiconductors do not have bound excitons.'

    ….. organic semiconductors are intrinsically unstable and organic light emitting diodes (OLEDs) will, therefore, never be reliable.'

    ….. organic semiconductors can't simultaneously transport electrons and holes.'

    ….. organic semiconductors will never show strong exciton-photon coupling.'

    ….. high charge carrier mobility and luminescence efficiency are mutually exclusive properties for organic semiconductors.'

Each one of these statements has proven to be wrong. There are plenty more statements that could also have been included in the list and one that we, and others, are currently working to challenge is that:

    ….. electrically pumped organic lasers are impossible.

The latter device, the organic laser diode, remains the one major device type that has not been achieved. The closest[32] anyone has come to a compact structure has been to use a high power pulsed InGaN LED to optically pump an organic DFB laser (like those

described by Professor Lemmer and Dr Laurand). Hopefully it will not be too long before this hybrid approach becomes unnecessary. Another promising result is the demonstration that electrically pumped resonant cavity OLED structrues can emit very narrow linewidths.[33] Even if these are not lasers, just as in the case of inorganic resonant cavity (RC-) LEDs, such RC-OLEDs offer many desirable features that for specific applications are likely to negate the need for a laser.

In conclusion, organic electronics and photonics remains an exciting research field in which to work with plenty of fundamental issues to consider and many opportunities to discover new phenomena and to develop new materials, devices and applications. The Faraday 174 Discussion Meeting organizers Professors Peter Skabara, Simon Higgins, Iain McCulloch, George Malliaras, Andy Mount and Ifor Samuel should be congratulated for assembling an excellent programme and all of the attendees and the RSC support staff should be thanked for helping to create a very lively and stimulating three days in a warm and sunny Glasgow. I very much enjoyed this, my first, Faraday Discussion Meeting.

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